THESIS

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MOHAMMAD. AHMAD. HASHMI

Department of Pure and Applied Chemistry

The University of Strathclyde,

Glasgow.

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SOME DIENYL COMPLEXES OF IRON

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SUMMARY

The work is based on the fact that cyclohexadiene and cycloheptadiene may be bonded to the transition metals like cyclopentadiene, by losing one hydrogen atom to give the respective 'π-dienyl' complexes. It is mainly concerned with studies of six and seven membered rings forming dienyl complexes with iron. Tricarbonyl-π-cyclohexadienyl iron II $C_6H_7Fe(CO)_3$ and tricarbonyl-π-cycloheptadienyliron $C_7H_9Fe(CO)_3$, (cations), isoelectronic with tricarbonyl cyclohexadienylmanganese(O), were treated with different nucleophilic agents, while efforts have also been made to prepare 'sandwich' type dienyl complexes of iron by nucleophilic hydride ion attack on cationic arene complexes.

Tricarbonyl-π-cycloheptadienyliron(II) tetrafluoroborate reacts with potassium iodide to give iododicarbonyl-π- cycloheptadienyliron. This known neutral compound gave tetracarbonyl-di-π-cycloheptadienyldiiron when treated with sodium. The related bridged compound, i.e. tetracarbonyl-π-cycloheptadienyl-π-cyclopentadienyl-di-iron was obtained by reaction of the same iodide with sodium cyclopentadienide. Cyanide ion also replaced the iodine and yielded cyanodicarbonyl-π-cycloheptadienyliron.

The reactions were applied to tricarbonyl-π-cyclohexadienyliron (II) tetrafluoroborate. They gave iodo-dicarbonyl-π-cyclohexadienyliron, which was further treated with sodium amalgam giving tetracarbonyl-di-π-cyclohexadienyl-di-iron, with sodium cyclopentadienide yielding tetracarbonyl π-cyclohexadienyl-π-cyclopentadienyl-di-iron and with potassium cyanide giving cyanodicarbonyl-π-cyclohexadienyliron.

In an attempt to find out the electrophilicity of the ligand, tricarbonyl-π-cyclohexadienyliron(II) tetrafluoroborate was reacted with phenyl-lithium, under different conditions. It gave only tetracarbonyl-di-π-cyclohexadienyl-di-iron and an unstable oil. This oil yielded tricarbonyl-π-cyclohexadienyliron(II) tetrafluoroborate on reaction with tritylfluoroborate. Further reactions of the cations with sodium methoxide and with the sodium salt of diethyl malonate afforded tricarbonyl-methoxy-cyclohexa-1,3-diene iron and tricarbonyl-di(ethoxylcarbonyl)methyl-cyclohexa-1,3-diene iron respectively. The same cation when treated with potassium cyanide in acetone gave tricarbonyl-cyanocyclohexa-1,3-diene-iron. All the above-mentioned nucleophiles are abstracted by trityl fluoroborate except the di(ethoxycarbonyl methyl group.

The same reaction scheme was followed with tricarbonyl-π-cycloheptadienyliron(II) tetrafluoroborate in the preparations of tricarbonyl-ethoxycyclohepta-1,3-diene iron, tricarbonyl (ethoxycarbonyl)methyl-cyclo heptadiene-iron and cyanocyclohepta-1,3-diene-iron. The structure of all these compounds have been fully discussed.

Iododicarbonyl-π-cycloheptadienyliron when refluxed in mesitylene in the presence of aluminium chloride gave the π-cycloheptadienyl-mesitylene-iron cation isolated as a reineckate and hexafluorophosphate.

The di-mesityleneiron cation was reduced by lithium aluminium hydride and sodium borohydride. It gave bis(trimethyl-π-cyclohexadienyl) iron. This method of production was tried on dibenzene-iron cation which

is unstable in water. An orange crystalline compound was obtained but could not be fully characterised due to the small yield. Both lithium aluminium hydride and sodium borohydride reduced mesitylene-π-cyclopentadienyliron triiodide yielding (trimethyl-π-cyclohexadienyl)-π-cyclopentadienyliron. Benzene-π-cyclopentadienyliron iodide did not react with sodium methoxide, the sodium salt of diethyl malonate or potassium tertiary but-oxide. However it does react with sodium borohydride and methyl lithium yielding cyclohexadienyl-π-cyclopentadienyliron and methyl-cyclohexadienyl-π-cyclopentadienyliron respectively.

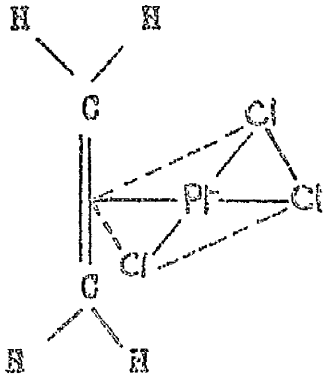
Certain electrophilic substitution reactions have also been attempted with π-cyclohexadienyl-π-cyclopentadienyl iron.

Dicarbonyl-π-cyclopentadienylcyclohexene iron hexafluorophosphate has been treated with different nucleophilic agents. Cyclohexyl-dicarbonyl-π-cyclopentadienyliron is produced when the cation is reduced with sodium borohydride. The compound is again converted into the original cation when reacted with trityl fluoroborate and into iododicarbonyl-π-cyclopentadienyliron and cyanodicarbonyl-π-cyclopentadienyl-iron when the cation is treated with potassium iodide and potassium cyanide respectively. The effect of other nucleophilic agents on this cation has also been studied.

CONTENTS

INTRODUCTION

One of the most significant developments in transition metal chemistry during the past decade has been the study of their organic complexes. The first organometallic derivative of a transition metal originated in 1827[1], when Zeise, a Danish chemist reported the preparation of a compound having the formula $Pt\ Cl_2C_2H_4$. This compound is now known to be a dimer with chlorine bridges; he also isolated a chloroplatinite with the ion $[C_2H_4Pt\ Cl_3]^-$ having structural formula I



(I)

Unsaturated hydrocarbons were known to be able to form such π-complexes with the halides of platinum metals and with those of copper, silver and mercury but in such compounds the bonding of the organic residue was thought to be either of a donar nature as in $(PtCl_2\ C_2H_4)_2$ or of a σ-bonded nature as in $Pt(CH_3)_4$ or CuC_6H_5. Inspite of the extensive research in organometallic chemistry during the period from 1830 to 1950, the preparation and study of organic derivatives of transition metals remained rather nebulous. It was generally held that transition metals were unable to form stable organic compounds. The early work along these lines is well summarised in the review by Cotton[2].

In such a state of affairs, the accidental discovery of the first "dienyl" complex of iron known as ferrocene, was a major and most exciting

development in organometallic chemistry. This unique compound was obtained first in 1951 by Kealy and Pauson[3] and then independently in 1952 by Miller, Tebboth and Tremain[4]. Following the revolutionary disclosure that the iron metal is equivalently bonded to the five carbon atoms of each of the cyclopentadienyl ligands; there has been a surge both of synthetic and theoretical activity in the field. Detailed studies on these derivatives in turn have contributed greatly to a better understanding of chemical bonding and it has been clearly recognised that formation of π-bonds to carbon is a characteristic property of all the transition metals.

During the past 15 years many other organic residues containing a π electron system have been shown to form metal derivatives, for example ethylene, the allyl group, various cyclobutadienes, arenes, cycloheptatrienes, cyclooctatetraenes and many others. When one considers the large number of potential π ligands and the fact that all the transition metals have now been found to form organometallic π complexes; this area certainly seems a new branch of chemistry.

In a very broad sense, all the organic derivatives of transition metals can be classified according to type of carbon-metal bonding as follows:-

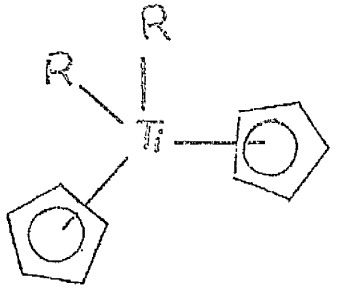
(a) Ionic complexes, in which the organic residue is anionic and is attracted to the metal cation by electrostatic force, e.g. Cp_2Mn

(b) σ-bonded complexes, where the organic ligand can be considered to donate one electron to the metal. It includes all the alkyl, acyl and

certain amyl complexes of transition metals, e.g. $Pt(CH_3)I$.

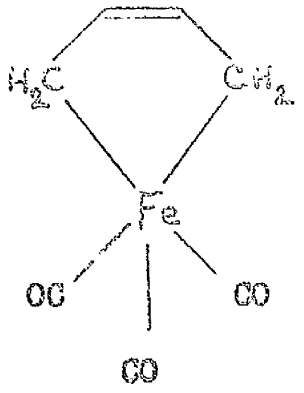
(c) π-bonded complexes; these complexes seem to involve electron sharing between the π-orbitals of the unsaturated system and the unfilled d orbital of the transition metals. The organic ligands donates 2 to 7 electrons to the metal as in the olefinic, enyl, diene and dienyl complexes.

However it should be emphasized that a particular transition metal complex may contain ligands bonded to the metal atom in different fashions, e.g. bis(π-cyclopentadienyl)-titaniumdialkyl exhibit both π- and σ-bonded ligands.



Open chain π-diene-metal complexes.

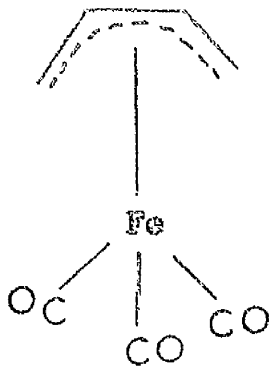
The study of diene metal complexes was initiated by Rheilen, Gruhl, Hessling and Pfrengle in 1930[5] when they reported the preparation of tricarbonyl butadieneiron. This compound is a pale yellow, diamagnetic, low melting solid of considerable thermal stability. For this compound they proposed the structure as II:-



(II)

Interesting results of the reaction of cyclopentadiene with iron pentacarbonyl prompted Hallam and Pauson[6] to reinvestigate the compound in order to obtain evidence on the structure. They found that the compound is unreactive towards catalytic hydrogenation and cannot be induced to undergo Diels Alder reaction. Therefore there is no evidence of a free double bond in the compound. The substance is so inert that it can even be recovered from concentrated sulphuric acid. Such a stability could not be expected from a complex containing two carbon atoms σ-bonded to iron. Moreover the structure would have only 34 electrons about the iron atom. Hence the compound would most probably be paramagnetic, whereas, as stated above it is diamagnetic.

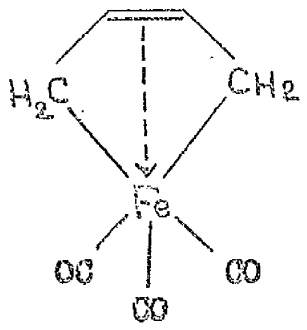
Therefore above structure II was rejected. By analogy with the theory of carbon-metal bonding in ferrocene they suggested another structure (III).



(III)

This structure implies that four carbon atoms of diene systems retain their Sp^2 state of hybridization upon complete formation of the compound. The bonding of the metal to the diene involves overlapping of suitable metal orbitals with the π-orbitals of butadiene as a whole.

In 1959 Green and coworkers[7] suggested another interesting structure and for the compound. These workers found that the n.m.r. spectrum of tricarbonyl butadieneiron shows three symmetrical complex bands, each of an intensity corresponding to two protons. The band at 5.28 p.p.m. is assigned to the two equivalent protons on the central carbon atoms. The bands at high field (1.68 p.p.m. and 0.22 p.p.m.) were assigned to the four protons on the terminal carbon atoms. The symmetry of all the band patterns showed that the terminal CH_2 groups are equivalent but that the two protons of each group are non-equivalent. This would be in accord with either Structure III or IV

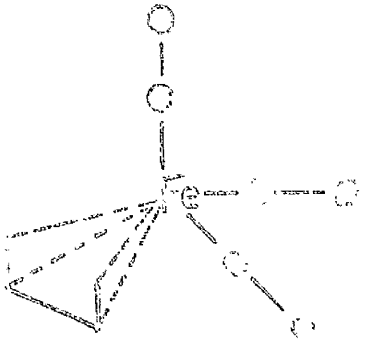


(IV)

The formula could not be approved due to the fact that infra-red stretching frequencies were of the C - H bonds and more like those associated with Sp^2 rather than with Sp^3 hybridized carbon-hydrogen bond favouring the formula III

From their studies Hallam and Pauson suggested that the following two requirements must be met by the diene in order that it may successfully form the diene metal tricarbonyl complex.

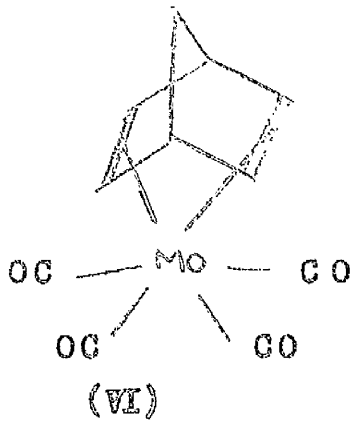
(i) The diene must be able to adopt cisoid conformation. In support of this requirement, they isolated tricarbonyl cyclohexadieneiron, almost identical in spectral and other properties with butadiene complex. Furthermore an x-ray study[8] of tricarbonyl butadieneiron confirmed Hallam and Pauson's conclusion,



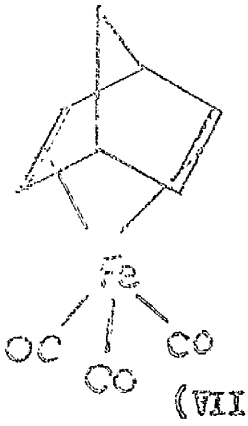
(V)

clearly showing that ligand is coplaner and cisoid but not coplaner with iron atom. It also confirms the delocalization of the π-electrons as the carbon - carbon bond lengths are equal (1.45 A).

(ii) The second suggestion put forward was that the diene must be conjugated. Inspite of the fact that the compounds like tricarbonyl bicycloheptadieneiron and analogous tetracarbonyl bicycloheptadiene molybdenum were prepared and related work by Wilkinson et al[9] showed that a suitable steriogeometry of the double bonds allows for the formation of non-conjugated diene-metal complex, still the vast majority of diolefinic-iron tricarbonyls are formed by conjugated dienes.



(VI)

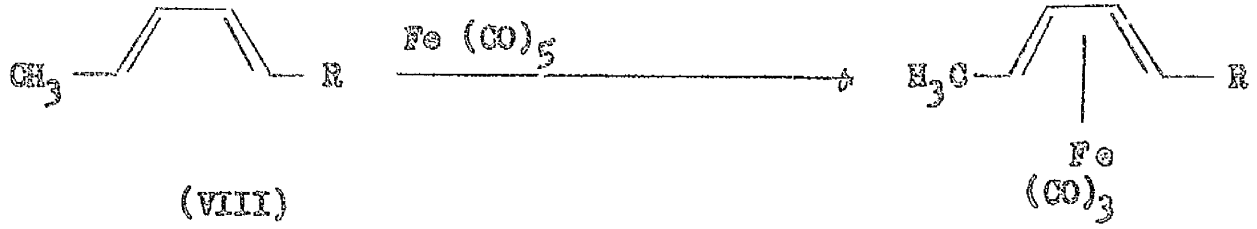


(VII)

Recently Stone and Co-workers[10] have reinvestigated the results reported by Reihlen et al[5] and confirmed that conjugation in a diene is really important for the existance of iron tricarbonyl complexes.

Regarding the stability of bicycloheptadiene metal carbonyls, it may be suggested that double bonds may be pulled together for overlap between the π-orbitals, so that in a reaction it may be regarded as a kind of conjugated dielefine.

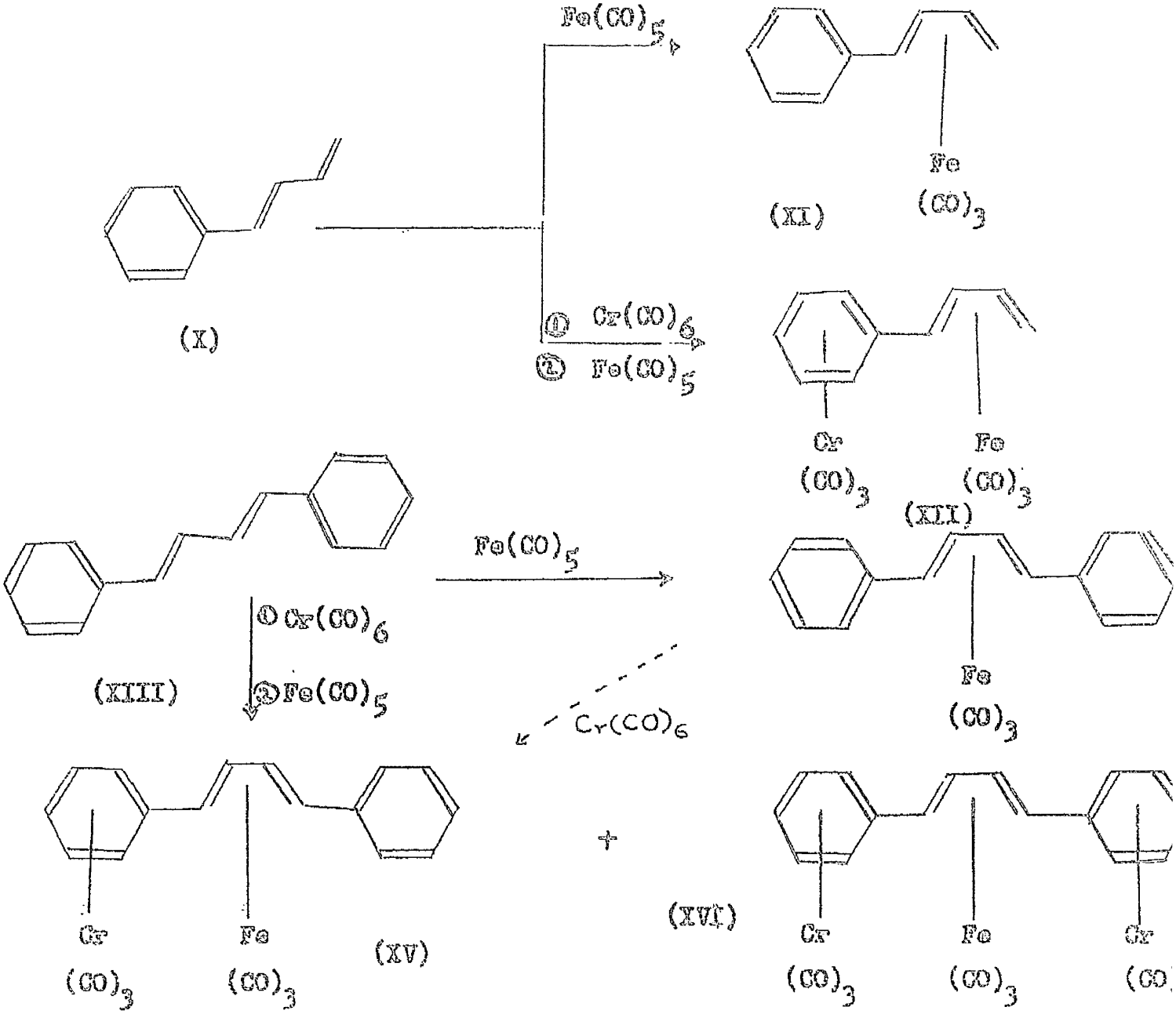
A series of derivatives of butadiene having general formula (VIII) have also been treated with iron pentacarbonyl to give the corresponding $Fe(CO)_3$ complexes



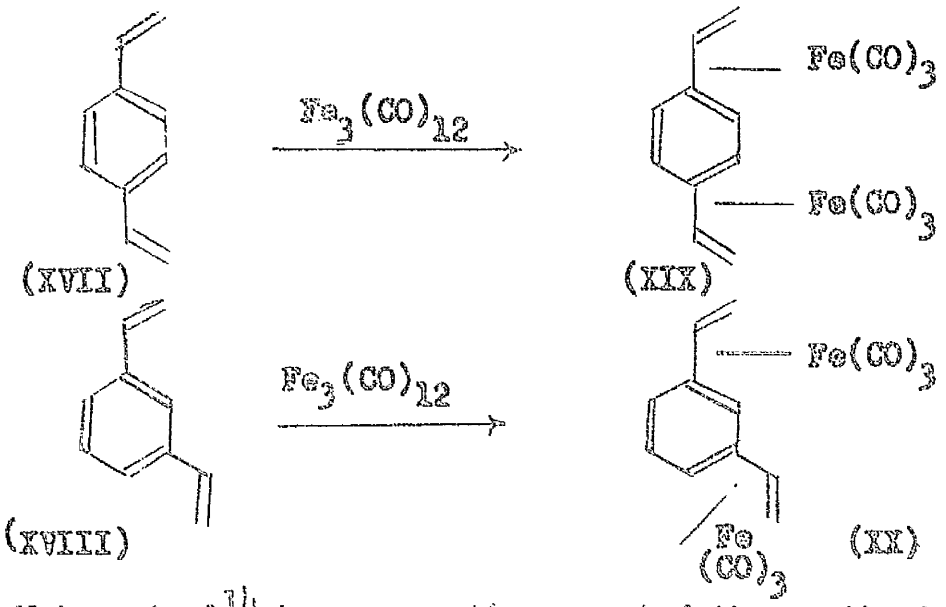
(VIII) (IX)

(R = - $CO_2C_2H_5$, - CO_2H, - CN, - $CONH_2$, - $COCH_3$, - CHO)

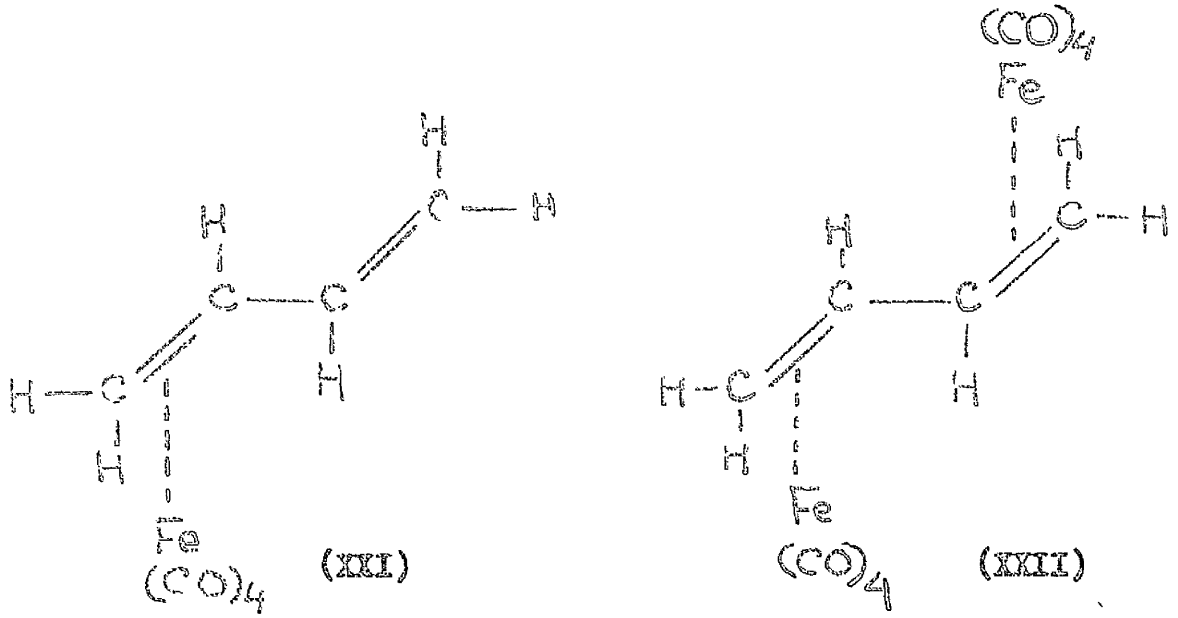
An interesting type of compound[11,12,13] has been obtained by the reactions between 1-phenyl-1,3-butadiene and 1,4-diphenyl-1,3-butadiene with iron carbonyl. 1,4-Diphenylbutadiene reacts with iron carbonyl givi yellow orange crystals of $C_4H_4(C_6H_5)_2Fe(CO)_3$. But 1,4-diphenyl functions as a benzene derivative in reactions with chromium hexacarbonyl and the substituted aromatic chromium tricarbonyl of composition $C_4H_4(C_6H_5)_2Cr(CO)$ or $C_4H_4(C_6H_5)_2\left[Cr(CO)_3\right]_2$ are formed, as is cleer from the following diagrams



m and p-Divinylbenzene also react in a similar way with dodecacarbonyl to form the respective complex as follows:-



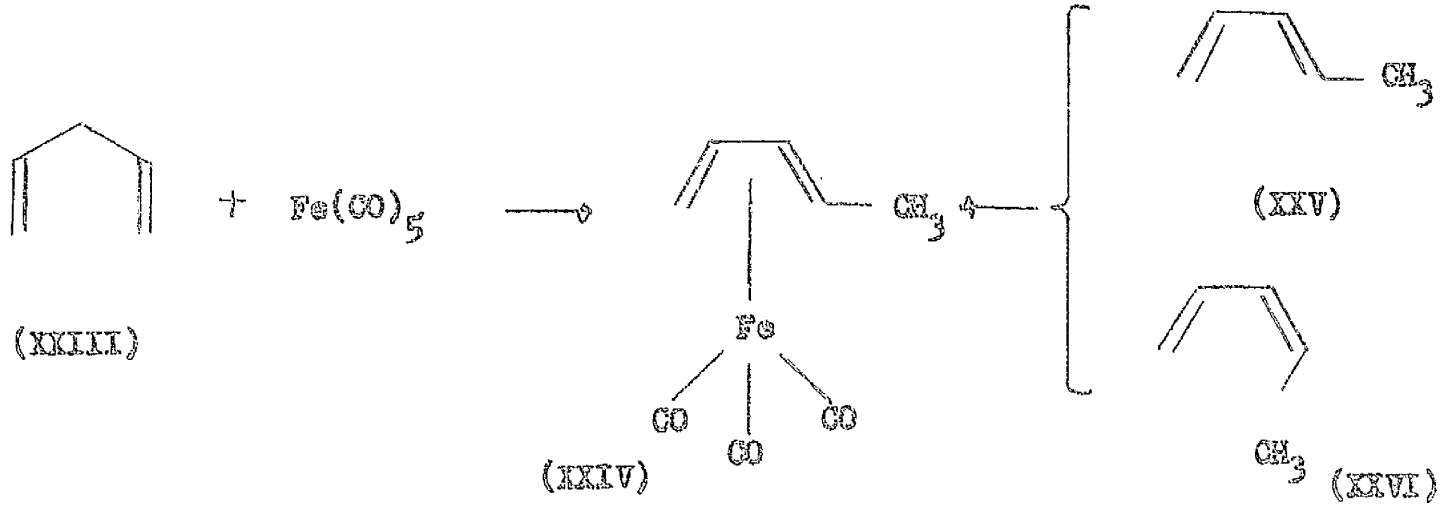
Weiss et al[14] have recently reported the synthesis of tetracarbonyl butadieneiron and octacarbonyl butadienediiron.



In such compounds the diene serves as a monofunctional ligand as in the cation $\left[C_5H_5Fe(CO)_2C_4H_6\right]^+$ [15]. Other butadiene complexes with other metals e.g. $(C_4H_6)_2\,Mo(CO)_2$, $\left[C_4H_6Co(CO)_2\right]_2$, $C_4H_6VC_5H_5(CO)_2$ and $C_4H_5Mn\,C_5H_5(CO)$ have also been prepared and studied.[16,12]

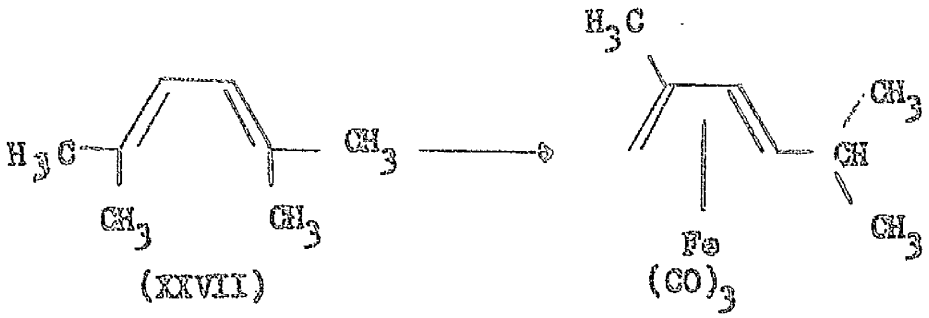
Many other acyclic dienes like 1,5-hexadiene and pentadiene complexes have been studied[18]. 1,5-Hexadiene gives rise to a mixture of tricarbonyls 1,3 and 2,4-hexadieneiron.

The reaction of 1,4-pentadiene (XXIII) with $Fe(CO)_5$ produces tricarbonyl trans-1,3-pentadieneiron (XXIV).

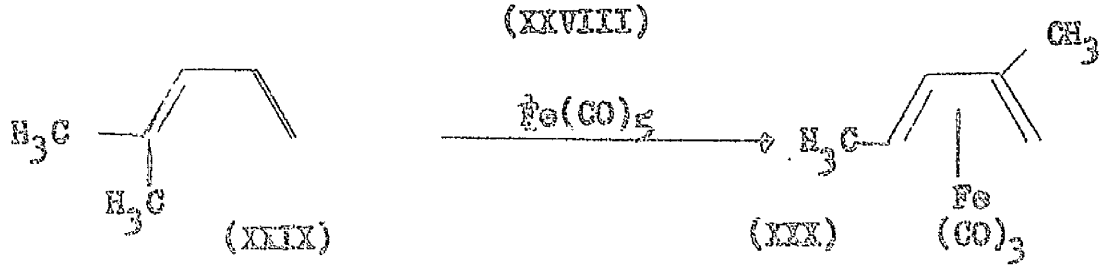


(XXIII) (XXIV) (XXV) (XXVI)

The same product is obtained when either trans-1,3-pentadiene (XXV) or cis-1,3-pentadiene (XXVI) is treated with iron pentacarbonyl. It has been generally observed that acyclicdienes having cis-alkyl substituents yield trans acyclicdieneiron complexes.



(XXVII) (XXVIII)



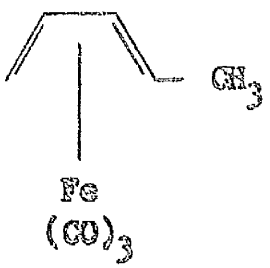
(XXIX) (XXX)

Acyclic Cationic Dienyl Complexes

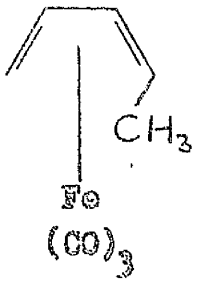
One important question which arises with the diene complexes concerns the reactivity of the diene ligand while bonded to $Fe(CO)_3$ relative to that of the free diene itself. Generally the dienes are much less reactive when complexed as is clear from Hallam and Pauson's[6] study of tricarbonyl butadieneiron.

However in one respect at least, the complexed diene is more reactive than the free dienes itself and this reaction involves the abstraction of a hydride ion from the carbon atom adjacent to the diene system. For example, Fischer[64] has found that the reaction of tricarbonyl cyclohexadieneiron with triphenylmethyltetrafluoroborate produced tricarbonyl cyclohexadienyliron tetrafluoroborate.

Petit et al[19] have studied acyclic dienyl cationic complexes



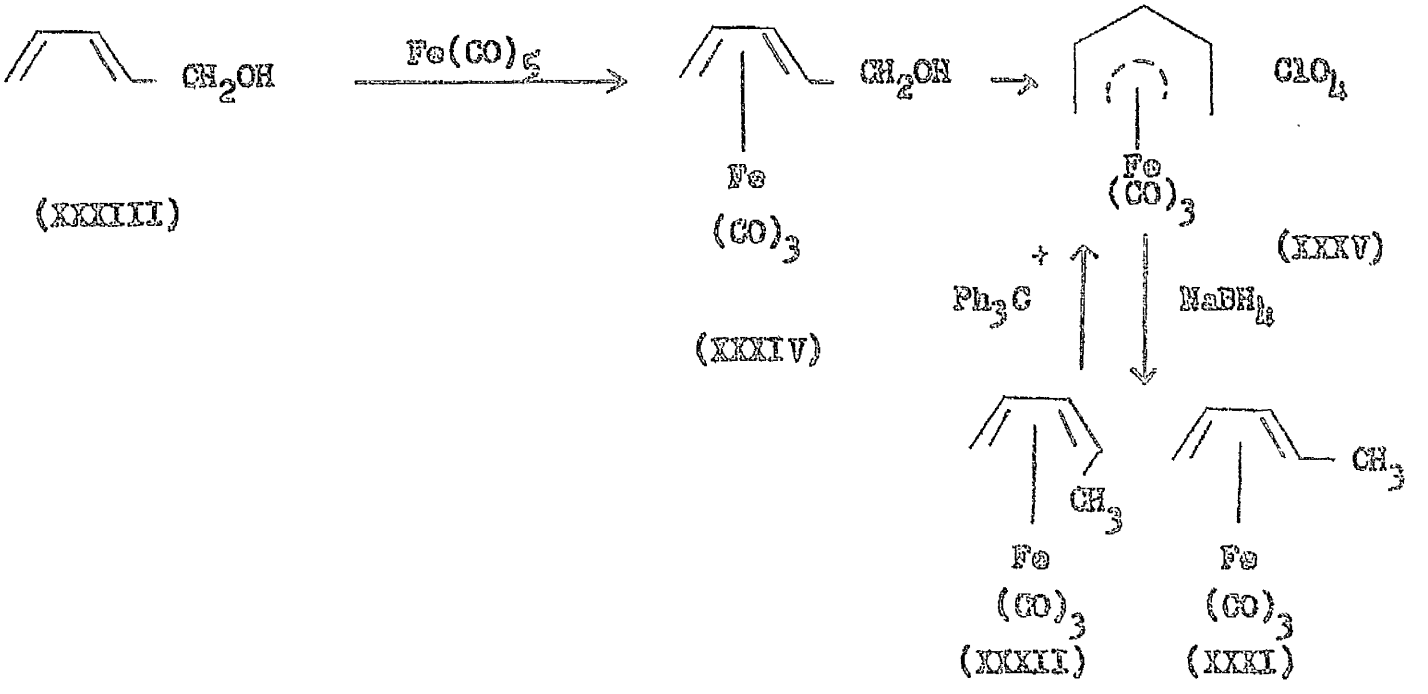
(XXXI)



(XXXII)

The triphenylmethyl cation fails to abstract a hydride ion from tricarbonyl trans-1,3-pentadieneiron (XXXI). Therefore the question arose whether cis-1,3-pentadiene (XXXII) would behave similarly. However at this stage this compound was not available as the reaction of cis-1,3-pentadiene with iron pentacarbonyl leads to the formation of the trans complex.

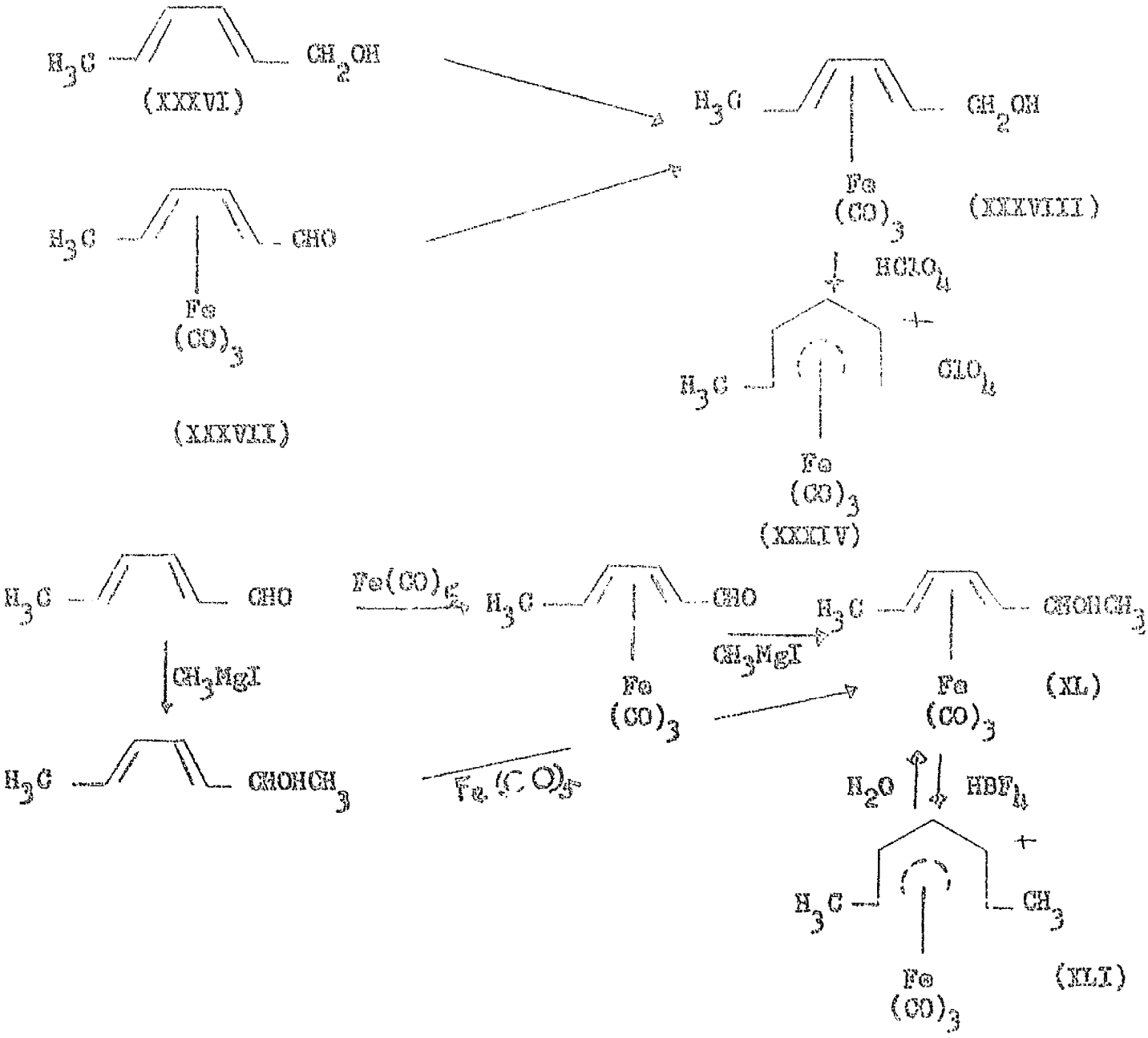
However the cis isomer has subsequently been obtained by an indirect route and it is found that the hydride abstraction reaction does proceed.



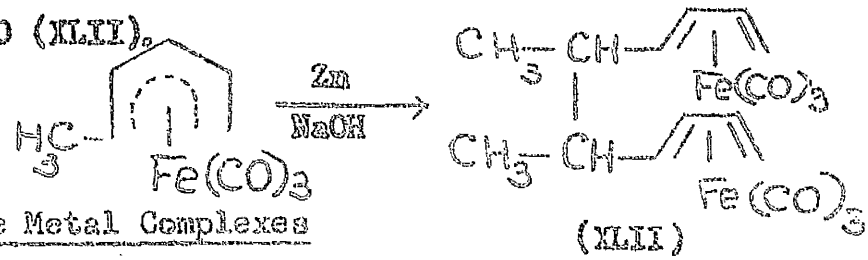
In view of the failure of the trans complex to undergo reaction with tritylfluoroborate, they treated tricarbonyl-trans-2,4, pentadiene-1-ol iron with perchloric acid. It gave an almost quantitative yield of the perchlorate salt of a tricarbonyl pentadienyliron cation. It has been shown that the cation possesses a cisoid structure rather than transoid ons. Other salts of cation (XXXV), e.g. the tetrafluoroborate and hexafluorophosphate are also formed. The salts are all yellow, crystalline diamagnetic solids, soluble only in polar solvent. They all possess strong carbonyl absorption in the infra-red at 2120 and 2072 cm^{-1}. The salts readily decompose in water to produce the trans alcohol complex. Treatment of the salts with sodium borohydride gives a mixture of the

stereoisomeric tricarbonyl pentadienoiron complexes. Degradation and n.m.r. studies of the mixture show that it comprises 80% cis and 20% trans isomer. In contrast to the trans, the cis isomer reacts readily with triphenylmethyl cation to give the salt (XXX/).

Tricarbonyl-1-methyl pentadienyliron and tricarbonyl-1,5-dimethylpentadienyliron cations have also been prepared via the reactio indicated in the following scheme.



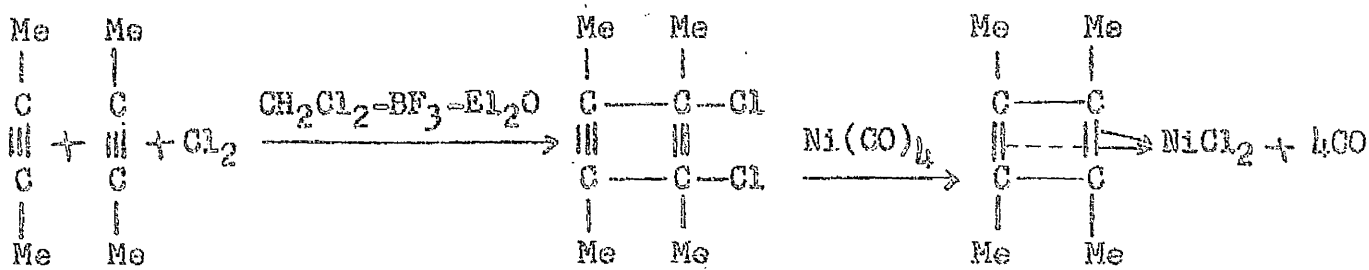
The same type of geometrical isomerism as in tricarbonyl trans-2,4-pentadiene-1-oliron, occurs upon formation of the cations and they are also seen in their reaction with water. Treatment of tricarbonyl-1-methylpentadienyliron cation with zinc or sodium hydroxide affords the bis (tricarbonyl) derivative of trans-trans-5,6-diemthyl-1,3,7,9-decatetraeneiron 0 (XLII),



(XLII)

π-Cyclobutadiene Metal Complexes

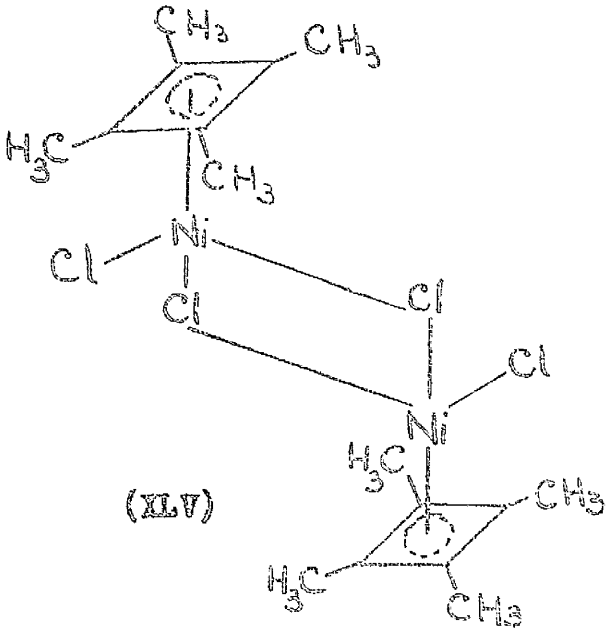
The synthesis of cyclobutadiene itself was an old problem for organic chemists. Efforts to prepare cyclobutadiene metal complexes started in 1956 when Orgel et al[20] predicted that stabilization of this organic entity was only possible by π-complex bonding to a metal. Criegle and Schroder[21] in 1959 succeeded in preparing the first π-complex of cyclobutadiene, i.e. tetramethyl cyclobutadiene nickel chloride according to the following scheme of reactions



XLIII XLIV

It is a red violet diamagnetic complex. This shows some unexpected properties, e.g. it forms an addition compound with chloroform and its

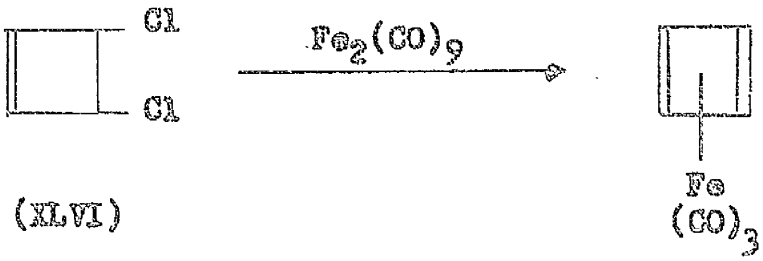
molecular weight is ten times that expected for a monomeric species[22]. The x-ray study[23,24] shows that in solid state the molecule is dimeric with the following structure



(XLV)

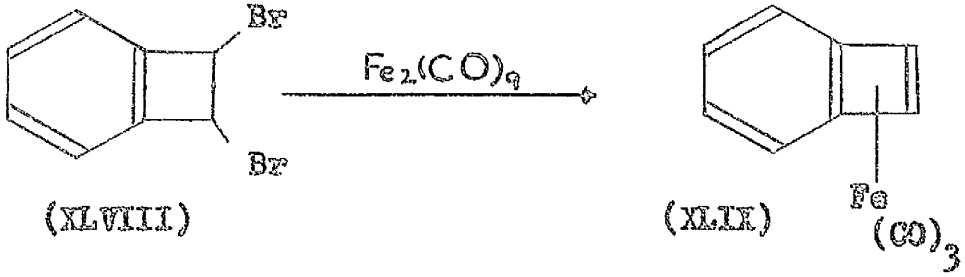
This behaviour with chloroform shows the tendancy of 5 co-ordinate nickel to make use of its vacant P orbital for bonding to various ligands. Tetraphenyl cyclobutadiene nickel di bromide[25] has also been prepared. It is very similar to the tetramethyl derivative. Tricarbonyl tetraphenyl cyclobutadieneiron was obtained by Reppe and coworkers[26] when they treated diphenyl acetylene with iron carbonyl in an inert solvent. This bright yellow solid, m.p. 234° , was further prepared in high yield by Weiss et al[27]. X-ray[28] study of the compound clearly shows the presence of the cyclobutadiene moiety and the phenyl group are twisted out of the plane of the ring and bent away from the $Fe(CO)_3$ group. Several tetraphenyl cyclobutadiene cobalt complexes of composition $C_5H_5CoC_4(C_6H_5)_4$, $[Co_4Hg_2(CO)_{12}(C_4(C_6H_5)_2H_2]$, $[Co_6Hg_3(CO)_{16}(C_4(C_6H_5)_2H_2)_2]$ and $[Co_2Hg(CO)_4(C_4(C_6H_5)_2H_2]_n$ have been prepared and studied[29].

Inspite of the fact that so many metal complexes of tetraphenyl and tetramethyl cyclobutadiene had been isolated and studied, no complex of cyclobutadiene itself was known until very recently, when Pettit and coworkers[30] reported the preparation of such a complex, namely tricarbonyl cyclobutadieneiron by the following route:



(XLVI) (XLVII)

They claim that the reaction can be utilized for the preparation of complexes of other cyclobutadiene derivatives. They also report the preparation of tricarbonyl benzocyclobutadieneiron in an analogous manner from trans dibromobenzocyclobutene and excess $Fe_2(CO)_9$. The structures

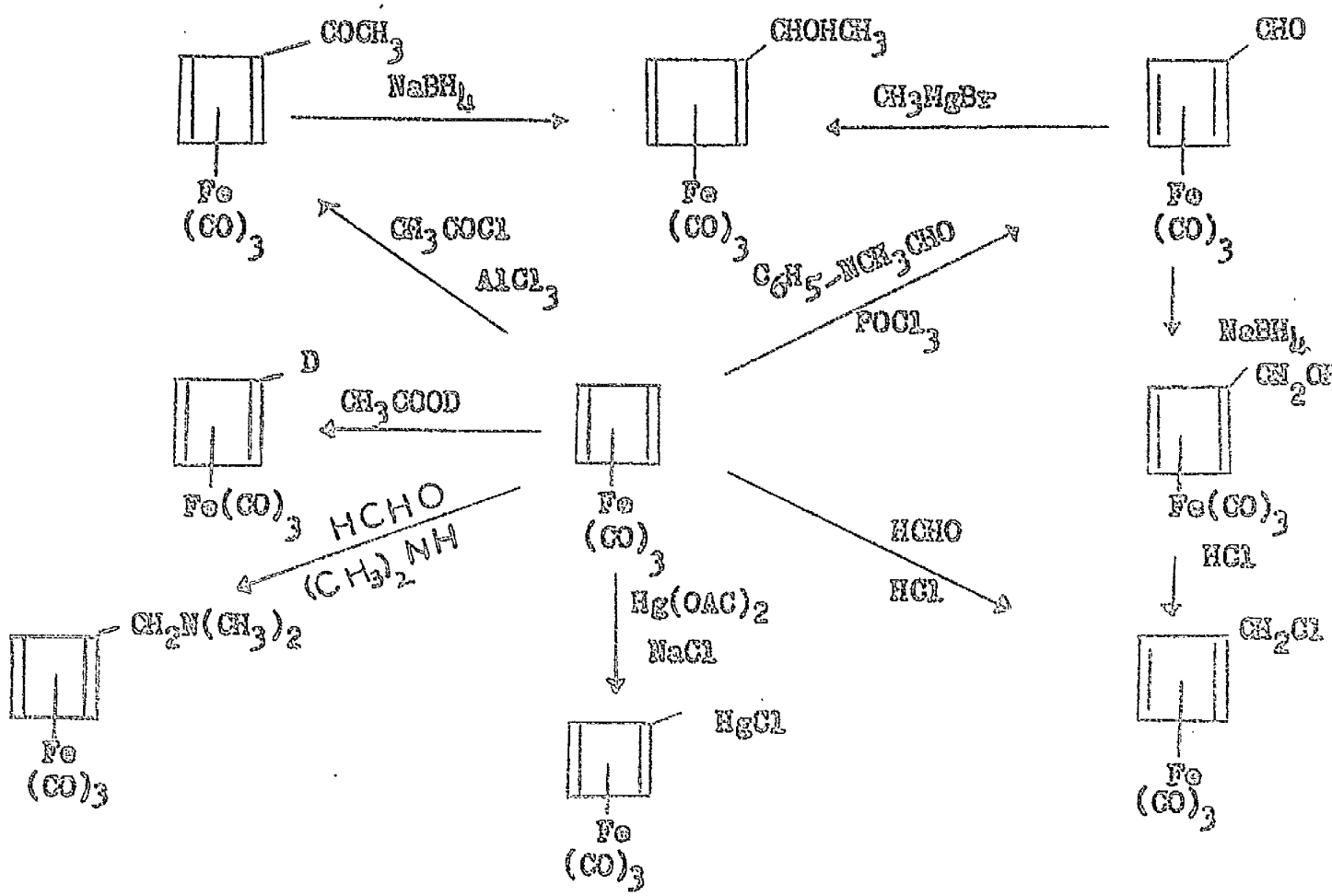


(XLVIII) (XLIX)

of both these compounds have been established by spectral and analytical data.

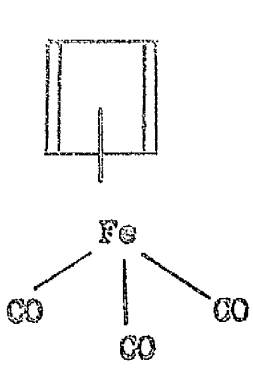
Pettit and coworkers[31] more recently demonstrated that tricarbonyl cyclobutadieneiron is an aromatic system in the sense that it undergoes electrophilic substitution reactions to yield a series of new

cyclobutadiene complexes. These reactions which are similar to the well known substitution reactionsof ferrocene are summarized as follows:-

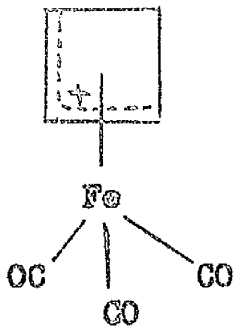


The n.m.r. spectra are in full accord with the assigned structures.

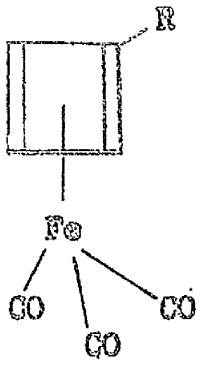
The aromatic character is readily rationalized in terms of the conventional mechanism operative for the electrophilic substitution of other aromatic systems such as benzene and ferrocene.



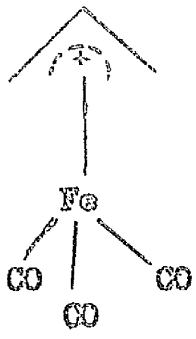
(XLVII)



(L)



(LI)



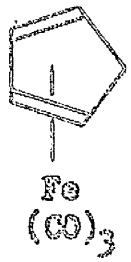
(LII)

Addition of an electrophilic species R^+ to complex (XLVII) can be envisaged as generating the π-allyl-tricarbonyliron cationic complex (L) stable salts of tricarbonyl - π-allyliron (LII) have already been isolated [32,33].

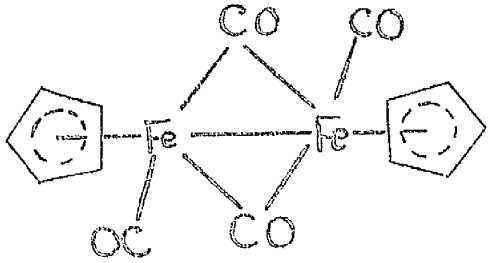
π-Cyclopentadiene Metal Complexes

The metal complexes of cyclopentadiene are of particular interest due to the fact that cyclopentadiene behaves quite differently from other conjugated dienes. It easily loses a proton to form the well known cyclopentadienyl complexes, e.g., the metallocene and related compounds [34,35,36]

Reaction of cyclopentadiene with iron pentacarbonyl does not afford compound (LIII) but instead yields

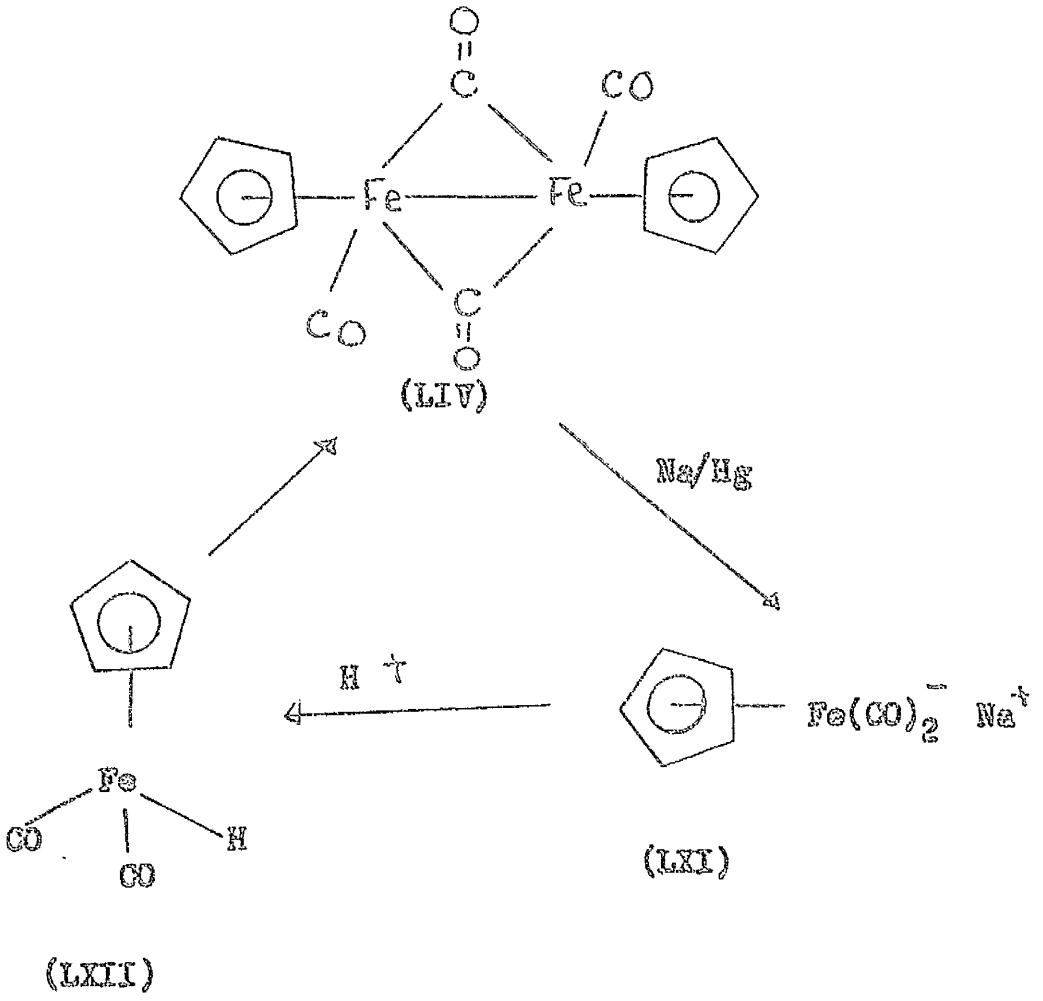


(LIII)



(LIV)

The following reactions[41] further prove the spontaneous decomposition of (LXII into the dimer (LIV)



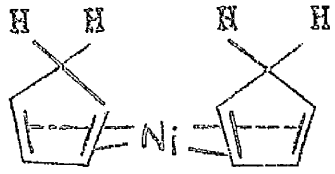
However there are many stable π-cyclopentadiene metal complexes reported in the literature[29].

Table I

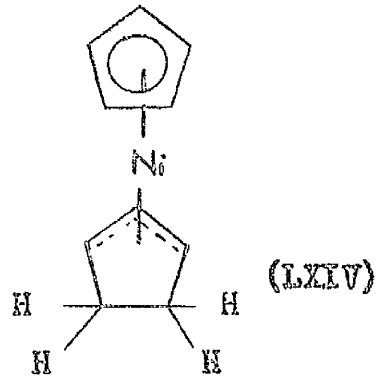
Cyclopentadiene-Metal Complexes

Compound	Properties	Reference
π-$C_5H_5Ir\ C_5H_6$	Bright yellow crystals, m.p. 130-132°	42
π-$C_5H_5Co\ C_5H_6$	Wine red crystals, m.p. 98,99°	44
π-$C_5H_5Co(C_5H_5CH_3)$	Red oil, m.p. $\sim$ -5°	44
π-$C_5H_5Co(C_5H_5CHCl_2)$	Orange red crystals, m.p. 50-51°	44
π-$C_5H_5Co(C_5H_5C\ Cl_3)$	Orange red crystals, m.p. 79-80°	44
π-$C_5H_5Co(C_5H_5CO\ C_6H_5)$	Red crystals, m.p. 125-127°	45
π-$C_5H_5Co(C_5H_5C_6H_5)$	Yellow red crystals, m.p. 128-129.5°	45
π-$C_5H_5Rh\ C_5H_6$	Orange yellow crystals, m.p. 121-122°	42,43

The reaction between cyclopentadiene and nickel carbonyl yields a red volatile, air stable, low melting solid, for which the structure (LXIII) was proposed



(LXIII)



(LXIV)

by Fischer et al[46]. The compound has been reformulated recently by various

groups of workers[29] independently as π-cyclopentadienyl π-cyclopentenyl nickel $C_5H_5Ni\ C_5H_7$ in which the cyclopentenyl radical is behaving as a three electron donor like the allyl radical. This structure has been proved on the basis of its n.m.r. It shows a sharp peak clearly assignable to the five equivalent protons of the π-cyclopentadienyl ring, together with peaks assignable to the three olefinic and four aliphatic protons of the cyclopentanyl ring[29].

Mixed cyclopentadiene-cyclopentadienyl metal complexes have been reported (Table 1). They have been prepared by two methods (a) $RhCl_3$ or $IrCl_3$ when treated with KC_5H_5 and excess cyclopentadiene yields the corresponding cyclopentadiene-cyclopentadienyl metal complexes[44].
(b) Reduction of the anhydrous cobalticinium and rhodicinium salts with sodium borohydride or lithium aluminium hydride

$$M(C_5H_5)_2^+ + H^- \longrightarrow C_5H_5\,M(C_5H_6)\ (M = Co,\ Rh)$$

In addition to the parent complexes, a series of substituted cobalt complexes have also been prepared from cobaltocene[44] or from cobalticinium salts[45] which are summarised below

$$(\pi\text{-}C_5H_5)_2Co \xrightarrow{CH_3I} (\pi\text{-}C_5H_5)_2Co^+I^- + \pi\text{-}C_5H_5Co(5\text{-}CH_3\text{-}C_5H_5)$$

$$(\pi\text{-}C_5H_5)_2Co \xrightarrow{CCl_4} C_5H_5Co(1\text{-}C\ Cl_3C_5H_5) \xrightarrow{LiAlHg} \pi\text{-}C_5H_5Co(5\text{-}CHCl_2C_5H_5)$$

$$\left[(C_5H_5)_2Co\right]^+ ClO_4^- + C_6H_5Li \longrightarrow C_5H_5Co(C_5H_5C_6H_5) + LiClO_4$$

Chemical studies reveal the presence of reactive hydrogen atom in the

$C_5H_5M\ C_5H_6$ compound. For example, the cobalt and rhodium compounds react with dilute acid giving the corresponding π-cyclopentadienyl metal cations and hydrogen and they react with carbon tetrachloride giving the same cations and chloroform

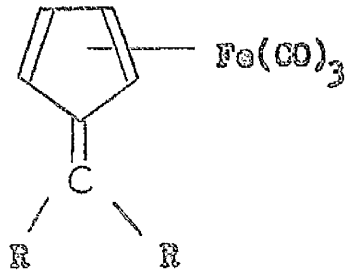
$$\pi\text{-}C_5H_5M\ C_5H_6 + H \longrightarrow (\pi\text{-}C_5H_5)_2M^+ + \tfrac{1}{2}H_2$$

$$\pi\text{-}C_5H_5M\ C_5H_6 + CCl_4 \longrightarrow (\pi\text{-}C_5H_5)_2M^+ + CHCl_3$$

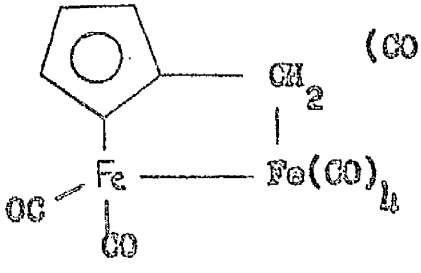
I.r. and n.m.r. spectra of such complexes have been extensively discussed[44,45].

The presence of an additional exocyclic double bond attached to the cyclopentadiene ring as found in fulvenes or cyclopentadienones allows the formation of stable metal complexes in which the cyclopentadiene moiety retains its conjugated diene character.

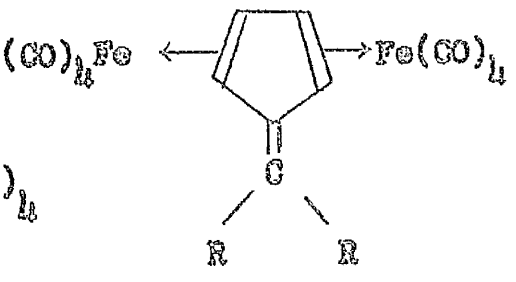
The reaction of fulvenes with metal carbonyls at high temperature (150°) yields substituted cyclopentadienyl metal carbonyl derivatives[47,48]. But by the use of milder thermal condition (40°) in the reaction between $\alpha\alpha$-disubstituted fulvenes and diironenneacarbonyl; Weiss and Hubel[48] have isolated $\alpha\alpha$ -disubstituted derivatives of tricarbonyl fulvenesiron.



(LXV)



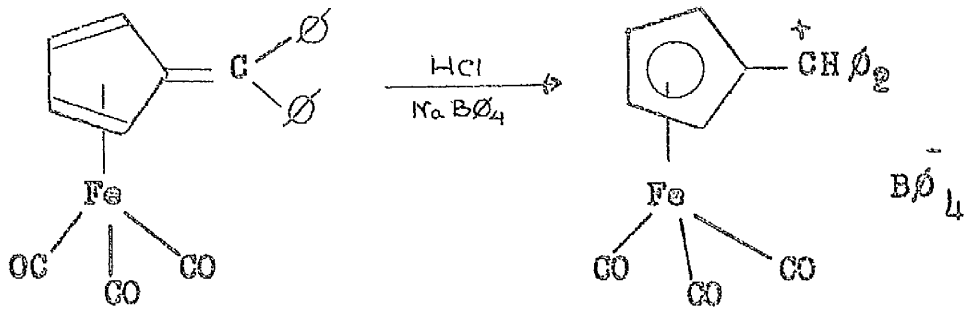
(LXVI)



(LXVII)

They have also reported[49] the preparation of an octacarbonyl fulvene-
They have also reported[49] the preparation of an octacarbonyl fulvene
diiron (LXVII) and hexacarbonyl fulveneiron for which the structure (LXVI) have been proposed.

The tricarbonyl fulveneiron complexes may be protonated to give substituted tricarbonyl cyclopentadienyliron cations, e.g.

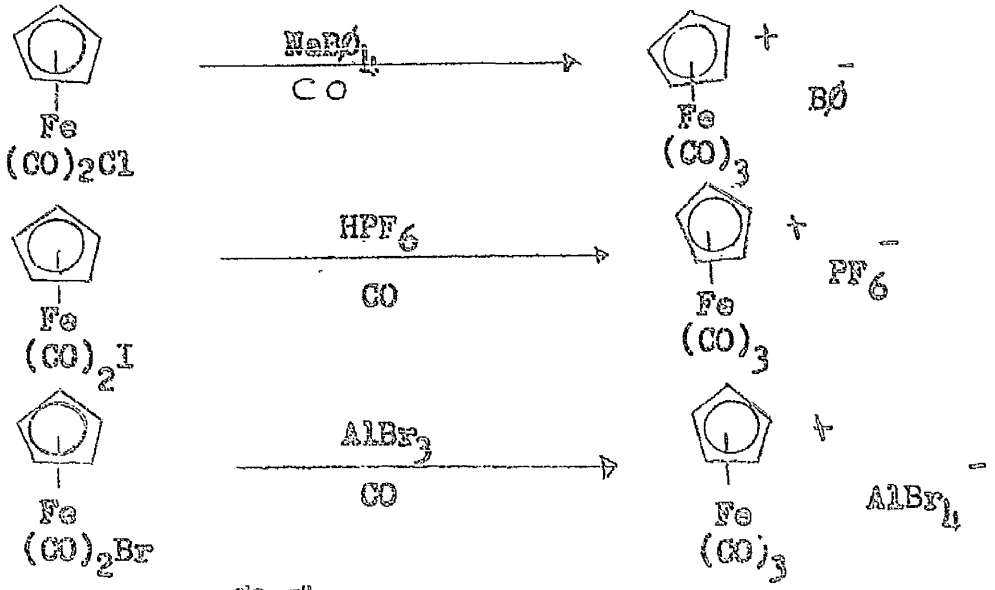


(LXVIII) (LXIX)

Regarding metal complexes of cyclopentadienone, it may be pointed out that cyclopentadienone itself is too unstable to be isolated and yet it forms stable metal complexes and this is another example of stabilization of an unstable olefinic species like cyclobutadiene by metal complex formation. The parent compound, tricarbonyl cyclopentadienoneiron is a yellow crystalline compound (m.p. 114-116°C). Complexes of cyclopentadienones of different transition metals have been described[50] and reviewed[29].

Cyclopentadienyl cationic complexes

Salts of tricarbonyl cyclopentadienyliron cations have also been prepared by different methods as outlined below[51,52,53]:-



Fischer and Fichtel[52,54] have also obtained salts of the cyclopentadienyl cationic complexes using ethylene in place of carbon monoxide

$$\pi\text{-CpM(CO)}_3\text{X} + \text{C}_2\text{H}_4 + \text{AlCl}_3 \longrightarrow \left[\pi\text{-C}_5\text{H}_5\text{M(CO)}_3(\text{C}_2\text{H}_4)\right]\ \text{AlX}_4$$

$$\text{M} = \text{Mo, W}$$

$$\pi\text{-CpFe(CO)}_2\text{Cl} + \text{C}_2\text{H}_4 + \text{AlCl}_3 \longrightarrow \left[\pi\text{C}_5\text{H}_5\text{Fe(CO}_2)\text{C}_2\text{H}_4\right]\ \text{AlX}_4$$

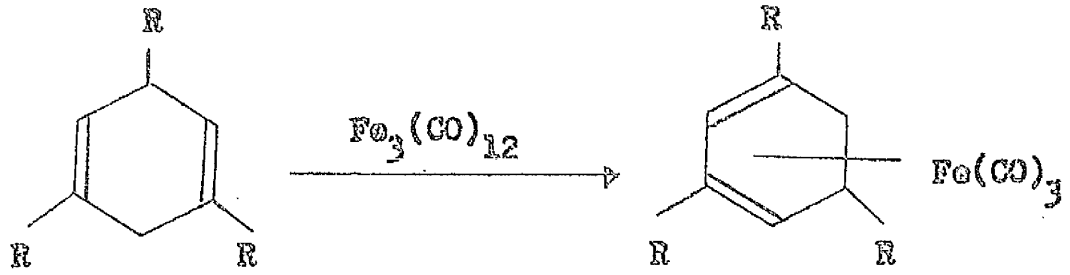
The cations have been isolated in the form of their salts with different anions, e.g. PF_6^-, $\left[Cr(NH_3)_2(NCS)_4\right]^-$. Several olefins, e.g. propylene, cyclohexene, butadiene, cyclohexadiene undergo similar reactions.

Table II

Cyclohexadiene Metal Complexes

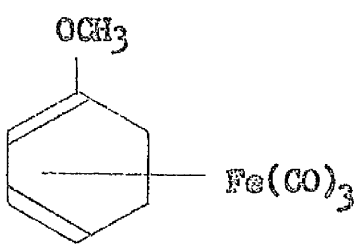
Compound	Properties	Reference
$C_6H_8Fe(CO)_3$	Yellow liquid, m.p. 8.9°	6
$C_6H_5Me_3Fe(CO)_3$	Yellow oil	10
$C_6F_8Fe(CO)_3$	Pale yellow crystals, m.p. 45°	55
$(C_6H_8)_2Mo(CO)_2$	Yellow crystals, d 90°	56
$Co_2(CO)_4(C_6H_8)_2$	Golden plates, d 100°	57,58
$C_5H_5V(CO)_2C_6H_8$	Dark red crystals, m.p. 98-100°	59

The study of cyclohexadiene metal complexes started in 1958, when the preparation of tricarbonyl cyclohexadieneiron was reported by Hallam and Pauson.[6] The importance of double bond conjugation is demonstrated by the reactions of 1,4-cyclohexadiene (R = H, CH_3) with $Fe_3(CO)_{12}$ which yields complexes containing the cyclohexa-1,3-diene ligand.

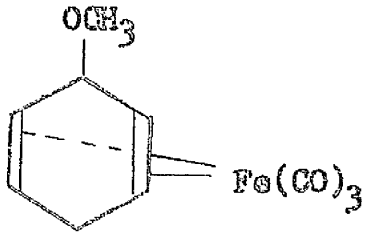


(LXX) (LXXI)

The reactions of octafluorocyclohexa-1,4-diene with trirondodecacarbonyl also gives a 1,3 diene derivative. The structure of such compounds have been discussed in the light of infra-red and n.m.r. data[60]. It is interesting to note that the reaction of 1-methoxy-cyclohexadiene with $Fe_3(CO)_{12}$ affords an equilibrium mixture of tricarbonyl, 1-methoxy cyclohexa-1,3-dieneiron (76% yield) and tricarbonyl-1,methoxy cyclohexa-1,4-dieneiron (24%). The mixture was characterized by its n.m.r.[61] spectrum.

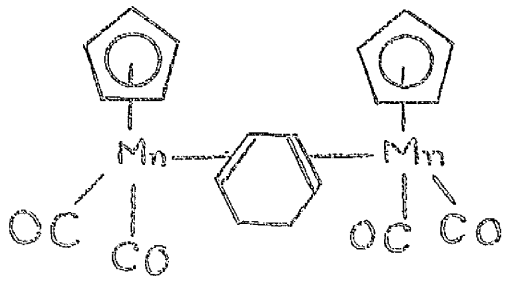


(LXXII)



(LXXIII)

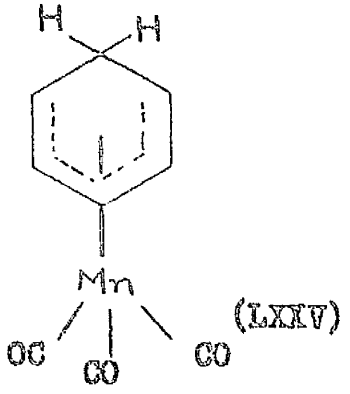
Fischer et al[59] have recently prepared several cyclohexadiene metal complexes by treating cyclopentadienyl complexes with cyclohexa-1,3-diene under ultraviolet irradiation, e.g. $C_6H_8VC_5H_5(CO)_2$, $C_5H_5MnC_6H_8(CO)$, $C_5H_5CoC_6H_8$ and $C_6H_8[C_5H_5Mn(CO)_2]_2$ have been prepared by this route. The last compound has the following structure



(LXXIV)

This is the first reported compound of a metal π-complex in which the cyclohexadiene molecule is incorporated as a bridge between two metal atoms.

In 1960 Wilkinson et al[62] quite unexpectedly reported that cyclohexadiene behaveslike cyclopentadiene, losing hydride ion, forming dienyl complex as the treatment of cyclohexa-1,3-diene with manganese carbonyl yields tricarbonyl cyclohexadienylmanganese. It is an extremely stable, yellow, volatile, diamagnetic complex

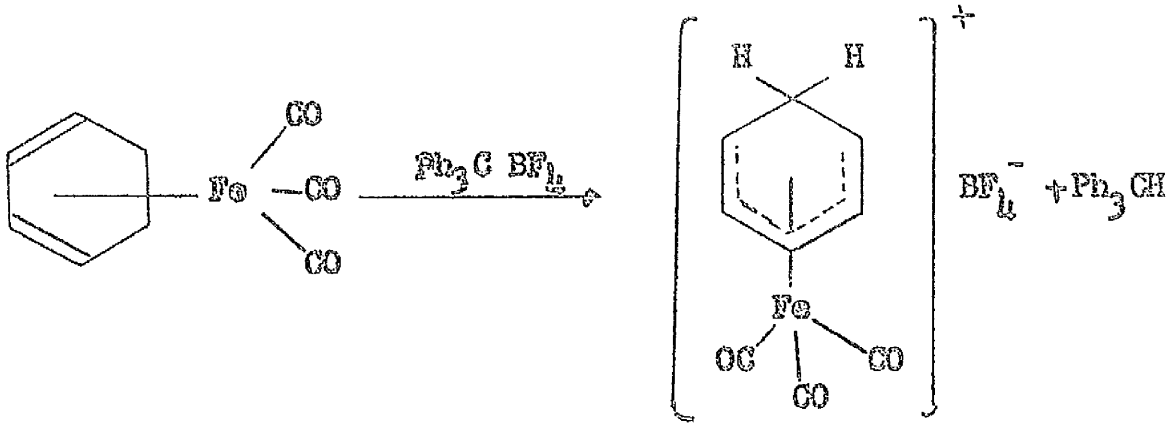


(LXXV)

The discovery of this compound paved a new way in the field of research. Tricarbonyl cyclohexadienylmanganese is even more readily obtained by reduction of $\left[C_6H_6Mn(CO)_3\right]^+$ with $NaBH_4$ in aqueous solution or with $LiAlH_4$ in ether. Substituted cyclohexadienylmanganese tricarbonyls are formed from the corresponding $\left[ArMn(CO)_3\right]^+$ cations (Ar = toluene mesitylene, hexamethylbenzene or naphthalene) by means of sodium borohydride[60].

Another route to prepare cyclohexadienyl metal complexes lies in hydride abstraction reaction. Fischer et al[64] prepared tricarbonyl cyclohexadienyliron tetrafluoroborate from tricarbonyl cyclohexa-1,3-

dieneiron by treating it with trityl fluoroborate



The cation is isoelectronic with tricarbonyl cyclohexadienylmanganese. It is a yellow, diamagnetic, air stable compound readily soluble in polar solvents.

DISCUSSION

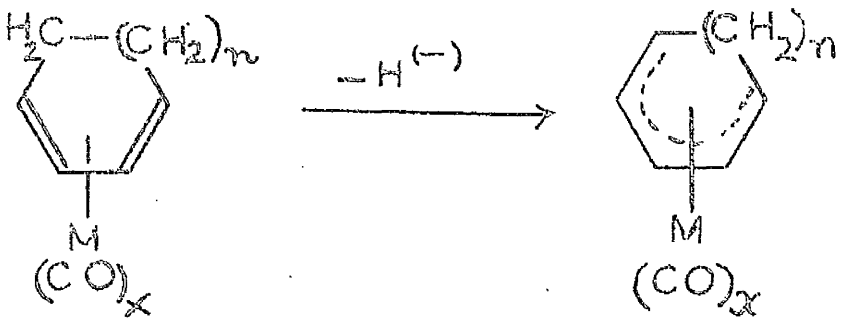
Since the discovery of tricarbonyl cyclohexadienyl manganese in 1961, several papers have been published concerning cyclohexadienyl complexes of Mn, Fe, Ru, Re[64,66-69]. However very little attention has been paid to the study of tricarbonyl cyclohexadienyliron cation salts[64] and their seven-membered ring homologues, tricarbonyl cycloheptadienyliron cation salts, just prepared by Dauben and Bertelli[70].

The work presented in this thesis is primarily concerned with the study of these cations.

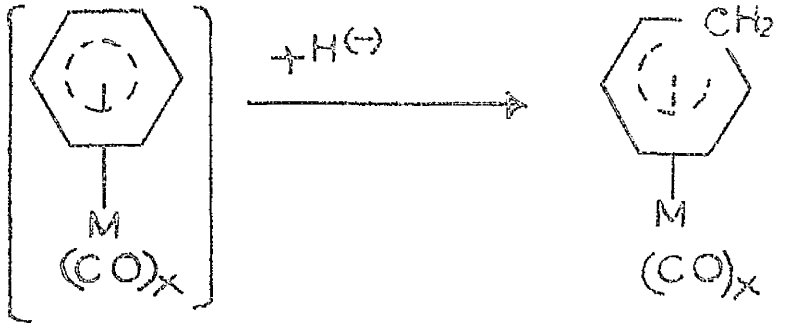
It is generally assumed that in such dienyl complexes, the carbocyclic ligands contain five sp^2 hybridised carbon atoms simultaneously bonded to the iron atom. They can thus be defined as complexes in which the organic ligands donate 5 electrons to the metal atom. Their stability is assumed due to the mode of bonding which involves the donor properties of the π-electron system of the ligand and back donation of electron density from the metal atom to the organic ligand through the interaction of filled d metalorbitals with vacant antibonding (π^*) orbitals of the carbonium ion ligand. This interaction is important since at the same time it strengthens metal-ligand bonding, decreases the electron density on the metal and concomitantly decreases the electrophilicity of the carbonium ion moiety.

Two general methods have been utilised to prepare such dienyl complexes. These are as follows:-

(i) Hydride ion abstraction from π-diene iron complex leading to a π-dienyl complex



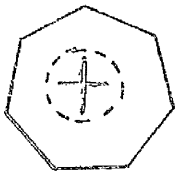
(ii) Hydride ion addition to arene metal cations



Both methods have been applied by the author to prepare dienyl complexes of iron.

The large numbers of cyclopentadienyliron complexes which have been prepared, prompted the investigation of the ability of the isoelectronic cyclohexadienyl and cycloheptadienyl ligands to form analogous iron complexes. The reactions of the complexes of these two isoelectronic cations, with suitable anions, were examined.

Tricarbonyl cycloheptadienyliron tetrafluoroborate [70]



LXXVII

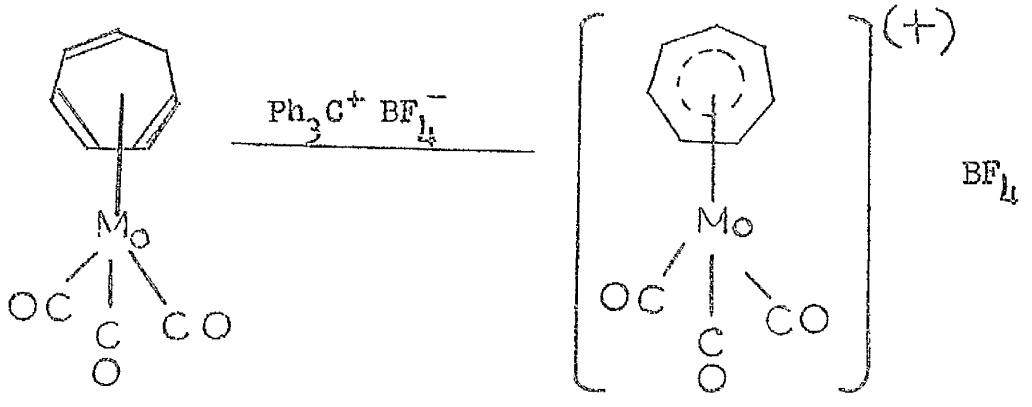
LXXVIII

LXXIX

The tropylium cation (LXXVII) is isoelectronic with the cyclopentadienyl anion (LXXIX) and with the neutral benzene nucleus (LXXVIII). Therefore in principle it should be able to form "sandwich" type complexes with transition metals.

When cycloheptatriene was refluxed with hexacarbonyl chromium or molybdenum, tricarbonyl cycloheptatriene chromium and molybdenum respectively were isolated[71].

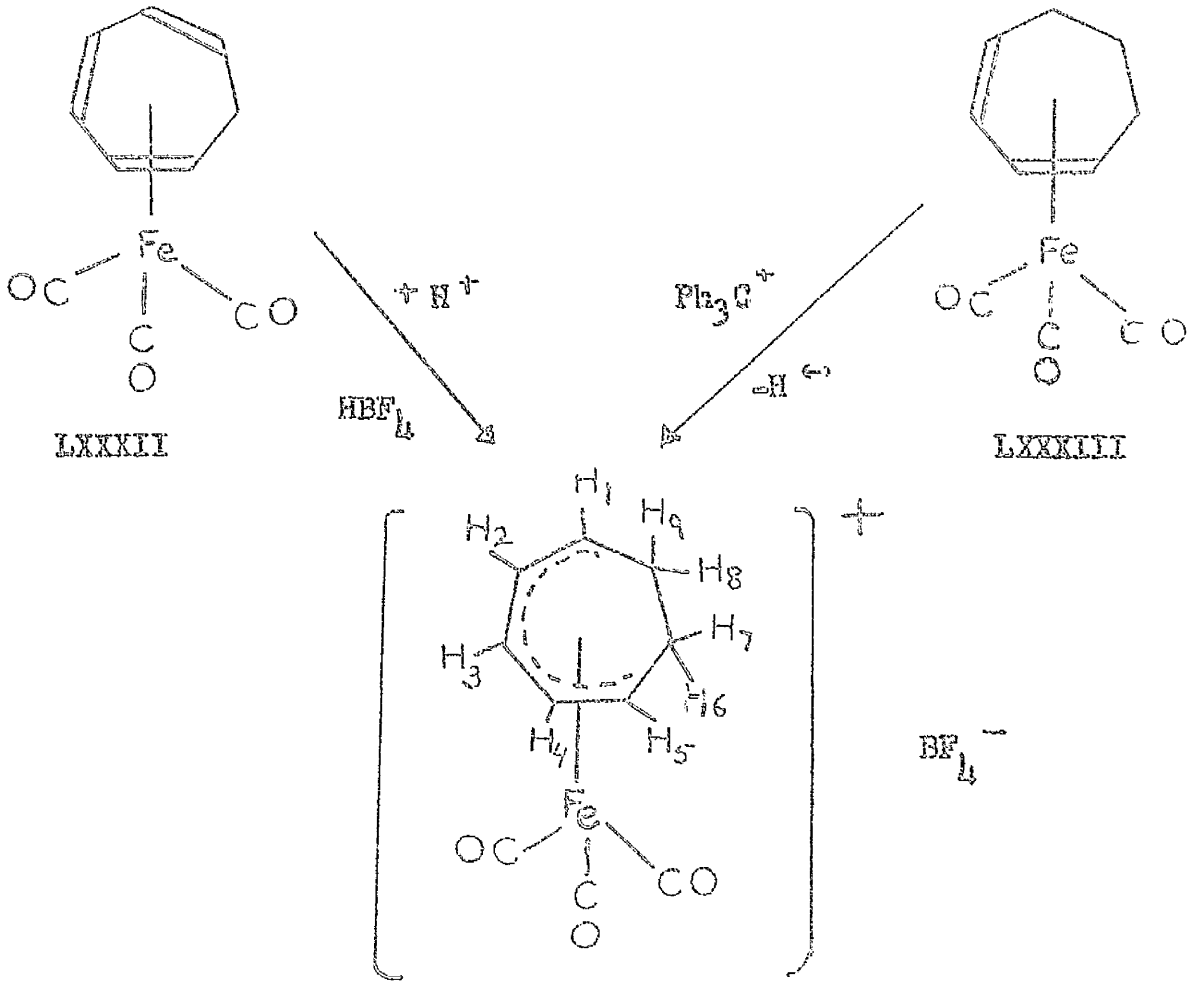
Dauben and Honnen synthesized first π-metal complex of the tropylium ion (LXXXI) by treating tricarbonyl cycloheptatriene molybdenum (LXXX) with trityl fluoroborate[75].



LXXX LXXXI

The reaction of cycloheptatriene with iron pentacarbonyl gave two products, the relative amounts of which depend on reaction conditions. Heating equimolar amounts of cycloheptatriene and iron pentacarbonyl at 135° for one day yielded a 19:1 ratio of $(C_7H_8)Fe(CO)_3$ (LXXXIII) and $C_7H_{10}Fe(CO)_3$ (LXXXII) respectively; whereas after five days the same products were formed in a ratio of 2:1 respectively.

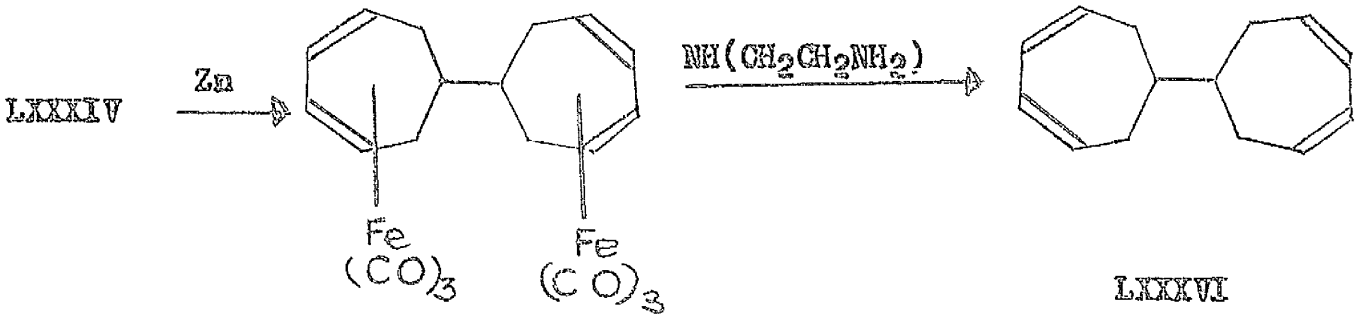
Tricarbonyl cycloheptadienyliron tetrafluoroborate was obtained by treatment of the cycloheptatriene complex with fluoroboric acid or by hydride ion abstraction from tricarbonyl cycloheptadiene-iron (LXXXIII) by triphenyl methyl cation.



LXXXII LXXXIII

LXXXIV

To confirm the structure of (LXXXIV), further reactions were carried out[65]. Reduction with sodium borohydride, lithium aluminium hydride and zinc dust respectively was investigated. Zinc dust promoted dimerisation of the cation (LXXXIV) to give the neutral complex (LXXXV) from which the corresponding hydrocarbon (LXXXVI) was



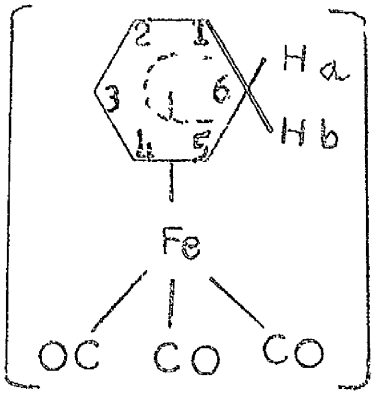
LXXXV

liberated on treatment with diethylenetriamine.

The fluoroborate salt (LXXXIV) is a stable bright yellow crystalline compound which darkens gradually above 150°. It displays metal carbonyl absorption at 2119(VS) 2062(VS) and 1980 cm^{-1} in the infra-red and the n.m.r. spectra contains resonances at τ,3.1(H_3), 4.2 (H_2,H_4), 5.2 (H_1,H_5), 7.5 (H_6,H_8) and 8.2 (H_7,H_9) (relative intensities of 1, 2, 2, 2, 2 respectively).[70]

Tricarbonyl cyclohexadienyliron tetrafluoroborate[64]

The tricarbonyl cyclohexadienyliron tetrafluoroborate was obtained in 80% yield by Fischer's method



BF_4

(LXXXVII)

The structure of the cation (LXXXVII) has been established by Wilkinson et al[67]. The n.m.r. spectrum of the compound gives the simple line pattern of a cyclohexadienyl system. The cyclohexadienyl ligand gives rise to three triplets of relative intensity 1:2:2, the triplet of unit relative intensity occuring at lowest field. These bands are assigned to the H_3(τ,2.66) H_2H_4(τ,4.08) and H_1H_5(τ,5.66) protons.

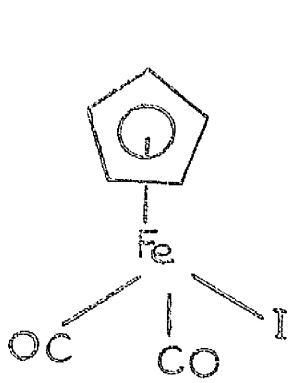
One of the two methylene protons gives two sharp bands at τ, 7.85 and 8.11 and the other gives two "triplets" at τ, 7.09 and 6.86. The difference in structure of the bands suggests that H_α and H_β are coupled in different ways to H_1 and H_5. This difference has been explained by assuming that the πC_6H_7 ring is not completely planer but that methylene carbon C_6 is bent out of the plane of the other carbon.

Iododicarbonyl π-dienyl iron

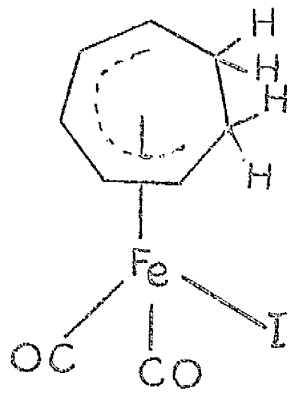
Many monomuclear π-cyclopentadienyl carbonyl metal halides, e.g. $C_5H_5Mo(CO)_3Cl$ $C_5H_5Fe(CO)_2X$ have been reported[80].

Chlorodicarbonyl cyclopentadienyl — iron was prepared by air oxidation of tetracarbonyl dicyclopentadienyldiiron in hydrochloric acid - methanol solution. The corresponding iodide (LXXXVIII), a black crystalline compound was obtained by heating the chloride with potassium iodide under reflux in ethanol solution.

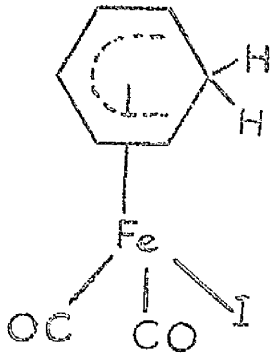
Dauben and Bertelli[70] have recently prepared iododicarbonyl cycloheptadienyliron (LXXXIX) by treating the tricarbonyl cycloheptadienyliron cation (LXXXIV) with potassium iodide in acetone. No



(LXXXVIII)



(LXXXIX)



(XC)

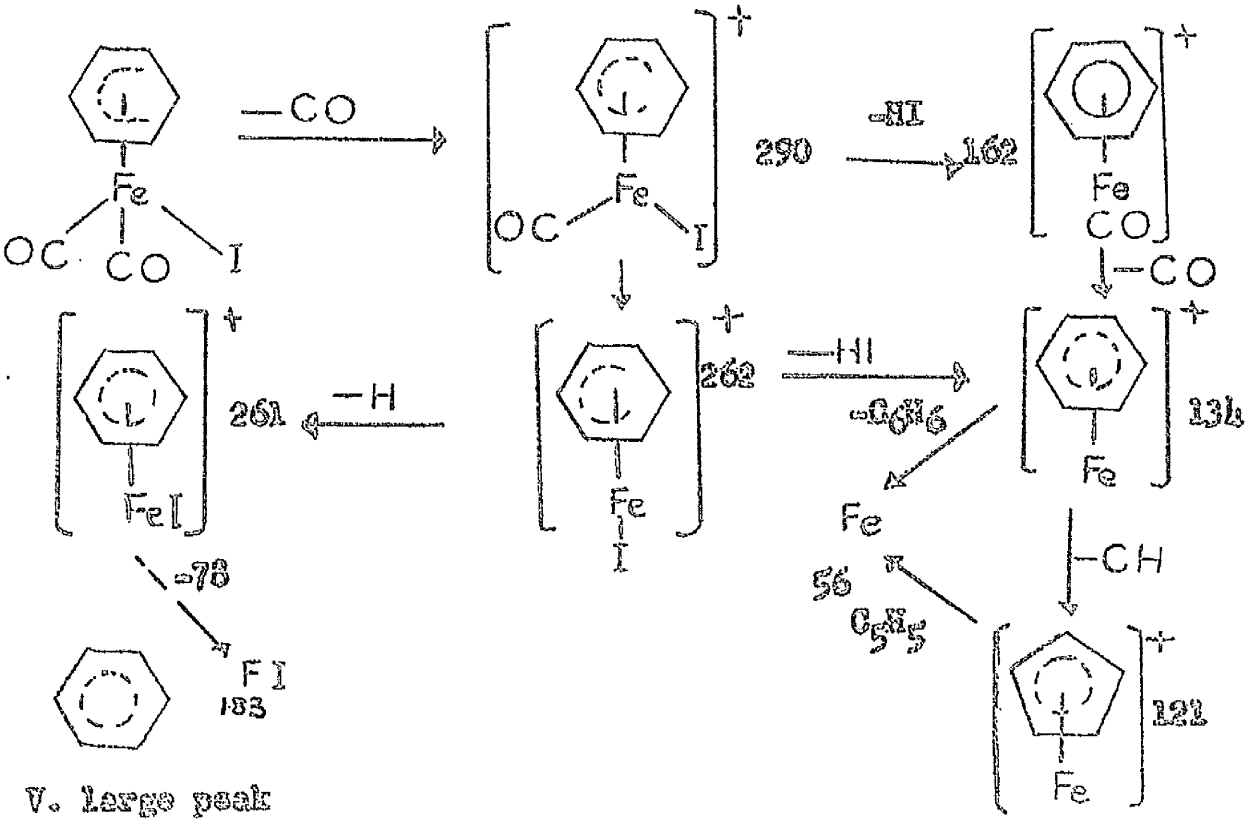
experimental detail was given.

The author prepared the six membered ring analogue (XC) in an analogous manner by treatment of tricarbonyl cyclohexadienyliron tetrafluoroborate with potassium iodide. The n.m.r. spectrum of the complex could not be obtained due to its unstability in solution. However its structure has been confirmed by analysis infra-red and mass spectroscopy.

The infra-red spectrum exhibits two sharp bands in the C-H stretching

region at 2941 and 2849 cm^{-1}. These bands can be attributed to the in-phase and out-of-phase vibrations of the two hydrogen atoms of the methylene group[99] in the cyclohexadienyl ligand of the complex. These bands may be compared with the infra red spectrum of tricarbonyl cyclohexadienyl-manganese in which these bands occur at 2970 cm^{-1} and 2830 cm^{-1}.(66) Its infra-red spectrum further contains peaks at 2041 and 1992 cm^{-1} in the metal carbonyl region as do its other dienyl-iron homologues. Lack of absorption in the 1550 - 1600 cm^{-1} region indicates the absence of a cyclohexadiene group and bands at 1445 and 1404 can be assigend to the C-C stretching modes of the ring.

Further evidence about the structure of the compound (XC) is derived from its mass spectrum which showed the following cracking pattern

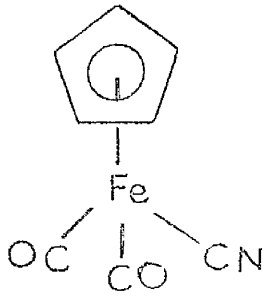


V. Large peak

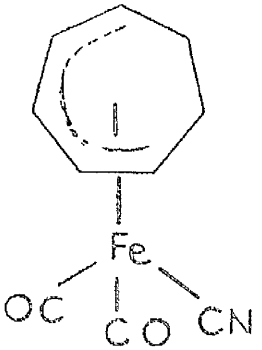
The physical properties of iododienyliron complexes of five, six and seven membered rings have been summarised in table 1. (See Appendix)

Cyanodicarbonyl π-dienyliron complexes

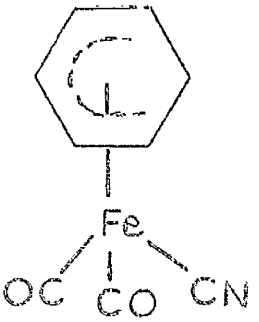
Cyanodicarbonyl cyclopentadienyliron[79] (XCI) was obtained by treatment of chloride carbonyl cyclopentadienyliron with sodium cyanide. In an analogous manner the six and seven membered ring dienyl complexes



(XCI)



(XCII)



(XCIII)

(XCII, XCIII) were obtained.

Treatment of iododicarbonyl cycloheptadienyliron (LXXXIX) with potassium cyanide in acetone afforded an orange crystalline compound (XCII) in 68% yield. The compound does not give a well defined nuclear magnetic resonance spectrum but its analysis and infra red spectrum confirm its structure as (XCII). The infra-red spectrum contains a sharp absorption at 2137 cm^{-1} characteristic of a cyanide group and the absorptions at 2040 and 1980 cm^{-1} in the metal carbonyl region are identical to those found with the compound (LXXXIX).

The reaction of iododicarbonyl cyclohexadienyliron with potassium

cyanide in acetone yielded cyanodicarbonyl cyclohexadienyliron (XCIII) as a pale yellow crystalline compound. The compound (XCIII) could not be rigorously purified due to decomposition during crystallization. Its structure, however, is established on the basis of its infra-red spectrum which is very similar to those of its five and seven membered ring homologues (XCI, XCII) whose structures have been unequivocably established.

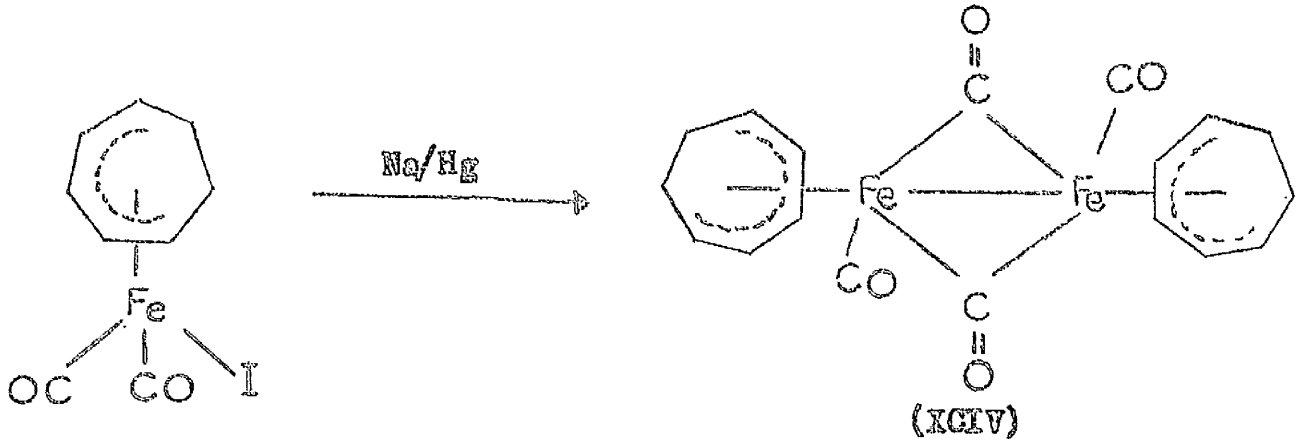
The infra-red spectrum contains two sharp peaks in the C-H stretching region at 2941 and 2817 cm^{-1} which can be assigned to symmetrical and antisymmetrical stretching modes of the methylene group in the cyclohexadienyl ligand (cf. 2926 and 2853 cm^{-1} $\pm$ 10 cm given by Bellamy for CH_2 group)[99]. The strong bands in the metal carbonyl region appears at 2941 and 1992 cm^{-1} and have identical frequency values to those of iododicarbonyl cyclohexadienyliron and tricarbonyl cyclohexadienyl manganese[63,67]. A significant sharp peak of medium intensity occurs at 2128 cm^{-1} which can be assigned to $-C\equiv N$ stretching frequency. Compounds having a cyano group attached to the ring have also been prepared. The difference in the frequencies of the stretching modes of the cyano group in such complexes will be discussed later.

Tetracarbonyldicyclic dienyl diiron

The first reported example of a dimeric dienyliron compound was $[C_5H_5Fe(CO)_2]_2$[79,81], obtained directly by interaction of iron pentacarbonyl and dicyclopentadiene. Aerial oxidation of the dimer in HCl or HBr afforded $C_5H_5Fe(CO)_2X$ (Cl or Br)[79,82].

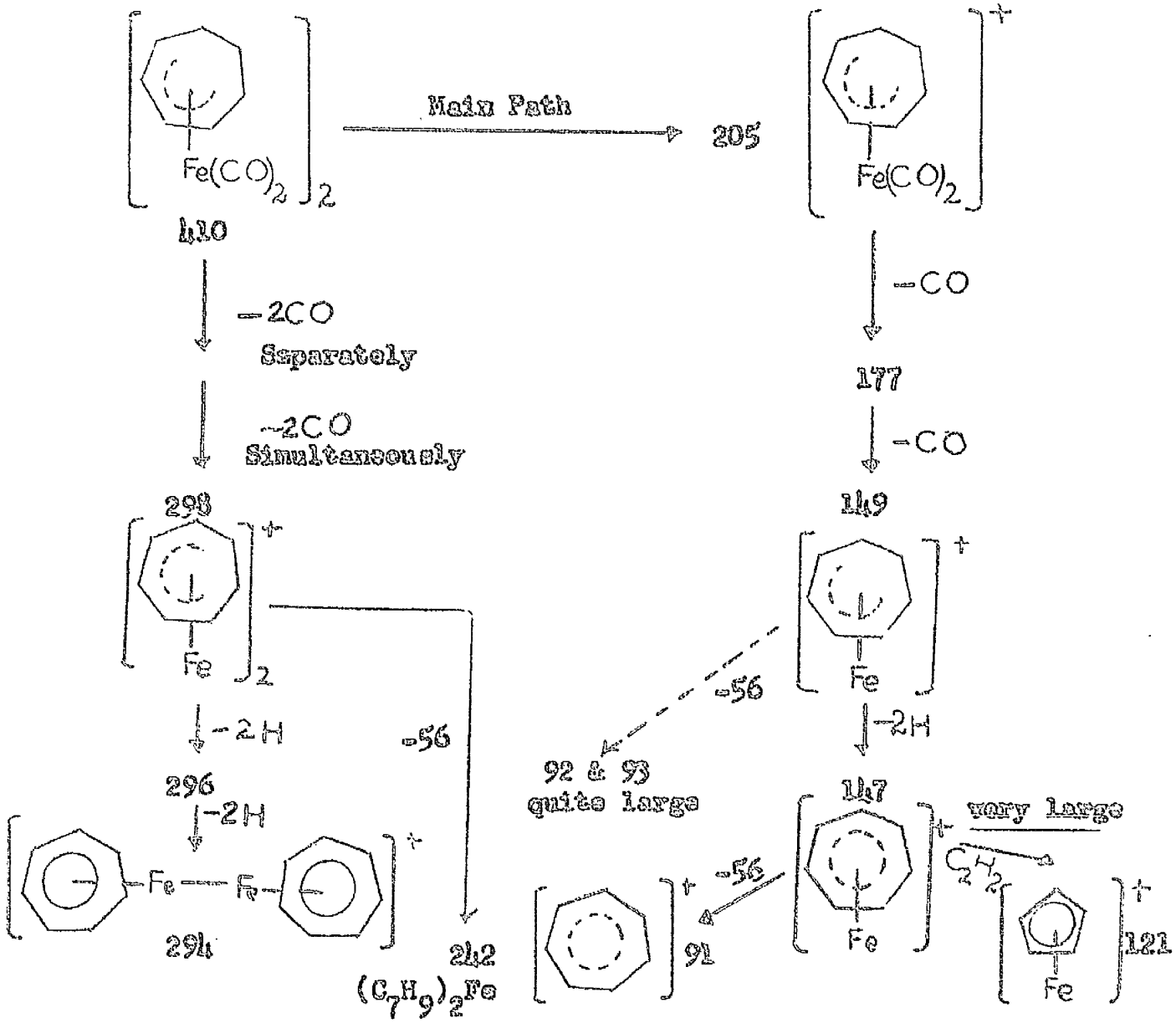
Assuming that the cyclohexadienyl and cycloheptadienyl ligands can donate 5 electrons to the iron atom in the same way as cyclopentadienyl group, the preparation of the analogous, six and seven membered ring dienyl dimers analogous to $\left[C_5H_5Fe(CO)_2\right]_2$ was attempted by reduction of iododicarbonyl dienyliron with sodium.

The compound (LXXXIX) on treatment with 1% sodium amalgum in tetrahydrofuran afforded bright red shining crystals of tetracarbonyl dicycloheptadienyldiiron.

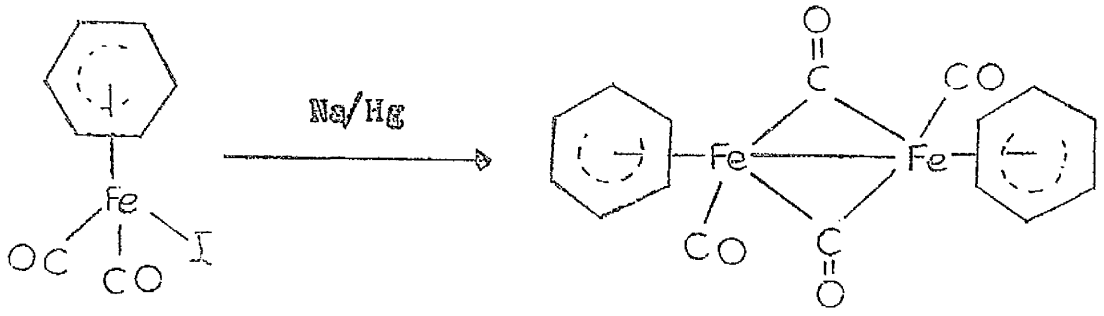


(XCIV)

The proposed structure (XCIV) of the compound was confirmed by analysis and spectral data. The infra-red spectrum is very similar to that of other dimeric dienyl iron complexes (see table 3 in Appendix). The mass spectrum shows the following cracking pattern.



Similarly treatment of iododicarbonyl cyclohexadienyliron (XC) with 1% sodium amalgum gave shining pinkish red crystals of tetra-carbonyl dicyclohexadienyldiiron (XCV)



(XCV)

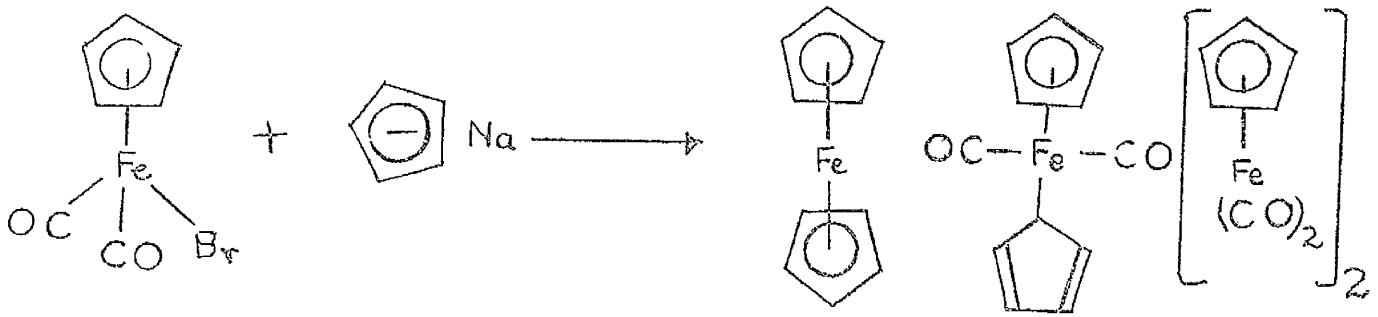
The compound has similar physical properties to compound (XCIV). Because of the marked instability of this complex, it was not obtained pure.

The structure of tetracarbonyl dicyclohexadienyldiiron (XCV) was established from the following infra-red evidence.

Absorption in the metal carbonyl and bridged carbonyl regions at 1976 and 1745 cm^{-1} respectively is unequivocal proof for the formation of dimeric structure. Other peaks characteristic of the cyclohexadienyl residue at 1401, 1316, 1297 and 1037 cm^{-1} [63,67] were also present.

Reactions of sodium cyclopentadienide with iododicarbonyldienyliron.

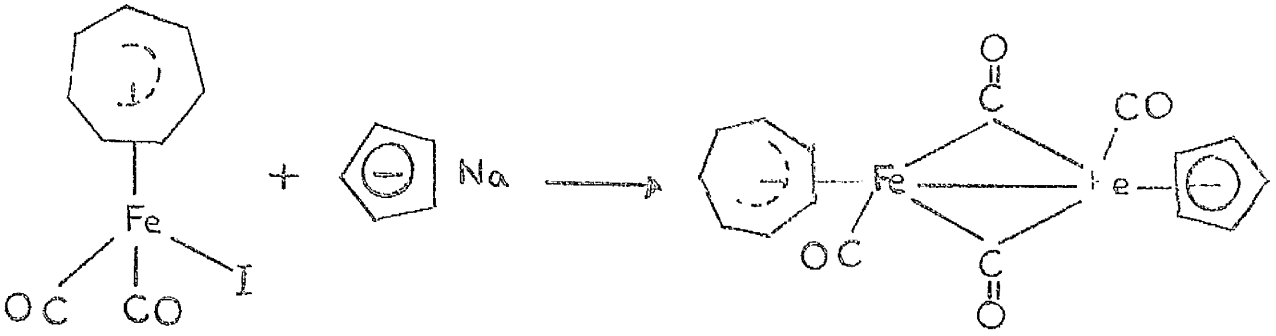
Hallam and Pauson[82] treated bromodicarbonyl cyclopentadienyliron with sodium cyclopentadienide and obtained an orange red crystalline compound (XCVI) which was originally reported as dicarbonyl dicyclopentadienyliron[83,84,85].



(XCVI) (XCVII)

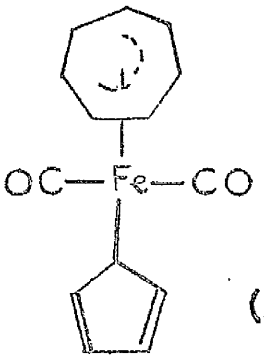
Ferrocene and dimer (XCVII) were also obtained as by products of the reaction.

In an analogous manner sodium cyclopentadienide was allowed to react with iododicarbonyl cycloheptadienyliron. A yellow crystalline product which spontaneously decomposed even under nitrogen was isolated. The brown residue was subjected to high vacuum sublimation since it was felt that some stable product might be obtained but no material could be obtained. The second product from the reaction, separated chromatographically was an orange red gum formed in a very low yield which was not identified. The unstable complexes may perhaps be the σ-cyclopentadienyl complex (XCVIII).



(XCIX)

The main product was identified as tetracarbonyl cycloheptadienyl cyclopentadienyldiiron (XCIX).

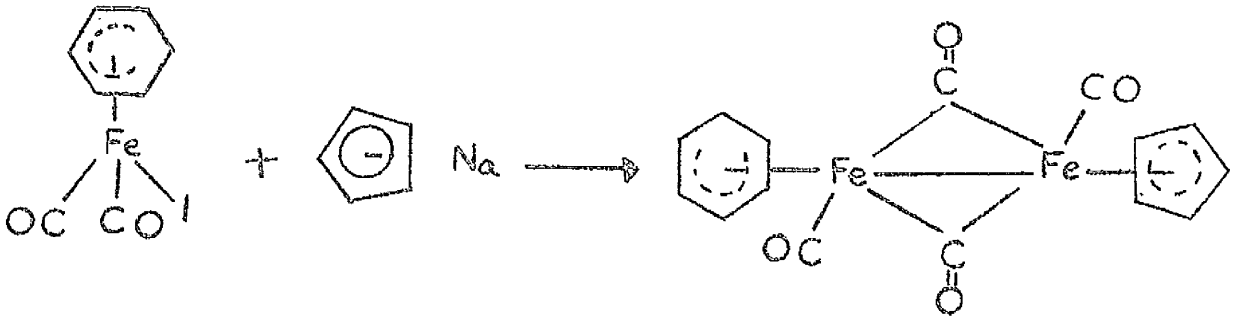


(XCVIII)

The compound was unstable in solution like the other bridged dienyl iron complexes. The proposed structure (XCIX) of the compound was supported by analysis and infra red spectrum. The n.m.r. spectrum could not be determined due to its instability and low solubility. The infra-red spectrum has been compared with those of other analogous complexes in table 3 (See Appendix). It contains metal carbonyl and bridged carbonyl absorptions at 1992 and 1751 cm^{-1}. The absorptions in the region from 3000 to 1000 cm^{-1} are very similar to those found with other analogous complexes.

The presence of the cyclopentadienyl group in the compound (XCIX) was confirmed by strong absorptions at 1422, 1360, 1110, 800-806 cm^{-1} which are characteristic of the π-cyclopentadienyl ligand.

Treatment of iododicarbonyl cyclohexadienyliron (XC) with sodium cyclopentadienide gave an analogous product, which again could not be characterised due to its low stability. This complex (C) was

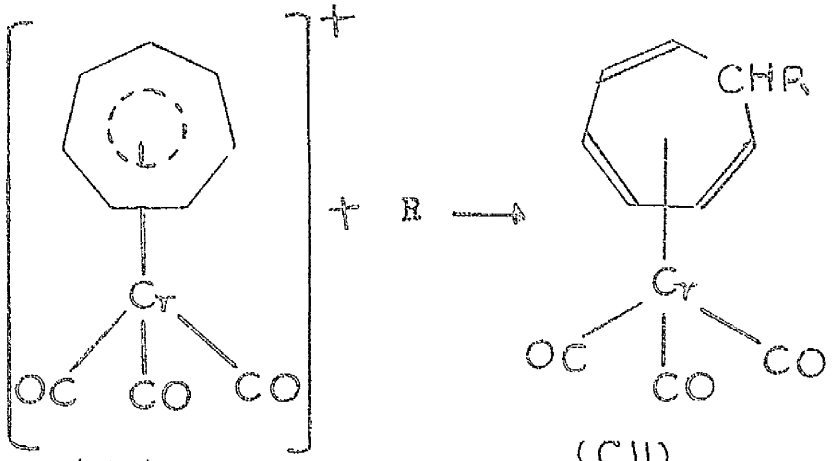


(C)

characterised only on the basis of the absorption in its infra-red spectrum in the carbonyl region at 1980 and 1770 cm^{-1} denoting metal carbonyl and bridging carbonyl groups.

Reactions of tricarbonyl cycloheptadienyliron and tricarbonyl cyclohexadienyiron cationswith anions.

Munro and Pauson[72,73,74] treated tricarbonyl π-tropylium-chromium cation with a variety of anions to establish whether the positive charge was localized mainly on the ring or alternatively on the metal atom. They



(CI) (CII)

assumed that such modes of reaction would be respectively I or II

I $\left[LM(CO)_3\right]^+ + X^- \longrightarrow XLM(CO)_3$

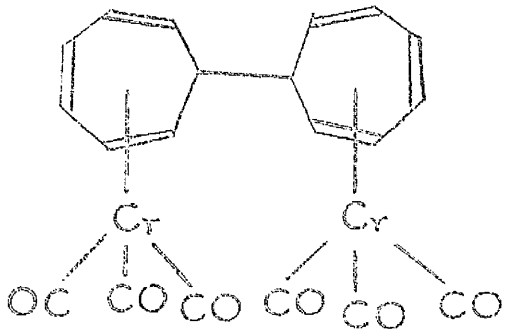
II $\left[LM(CO)_3\right]^+ + X^- \longrightarrow LM(CO)_2X + CO$

It was shown that many anions such as $H^{(-)}$, $\overset{(-)}{O}CH_3$, $\overset{(-)}{S}H$, $C_5H_4\overset{(-)}{C}(CH_3)_3$, $\overset{(-)}{C}CH_3(CO_2C_2H_5)_2$ specifically attack the seven membered ring suggesting that the positive charge resides largely on the ligand[72].

However the reaction of tricarbonyl tropylium-chromium perchlorate (CI) with cyclopentadienide anion , an ion with strong affinity for transition metals does not produce a cycloheptatriene complex of the type (CII) nor does the anion attack the metal. This reaction was found to lead to contraction of the seven membered ring with resultant

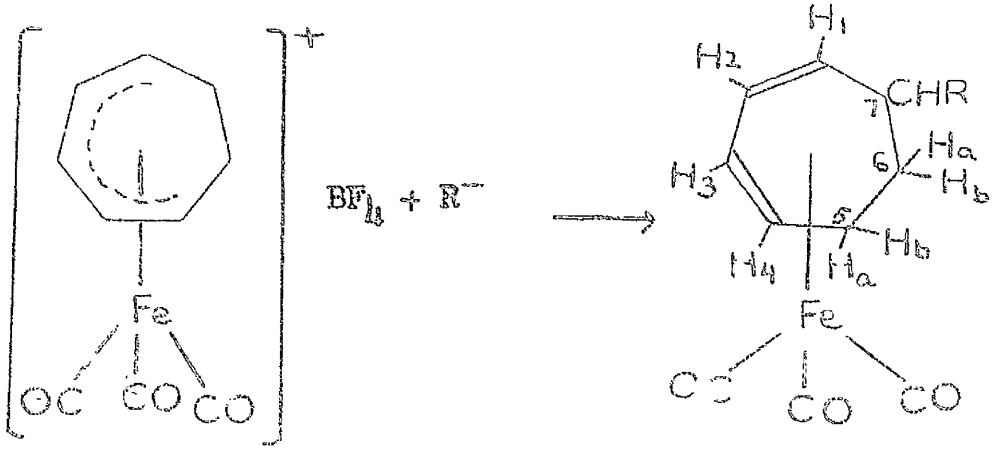
formation of tricarbonyl benzene-chromium.

A quite different result was obtained when the compound (CI) was treated with cyanide ion. In addition to a small amount of the expected derivative (CII, R = CN), the main product obtained from the reaction was shown to have the structure (CIII).



(CIII)

This interesting behaviour with different anions prompted the author to examine the reactions of the tricarbonyl cycloheptadienyliron (LXXXIV) and tricarbonyl cyclohexadienyliron (LXXXVII) cations with various anions.



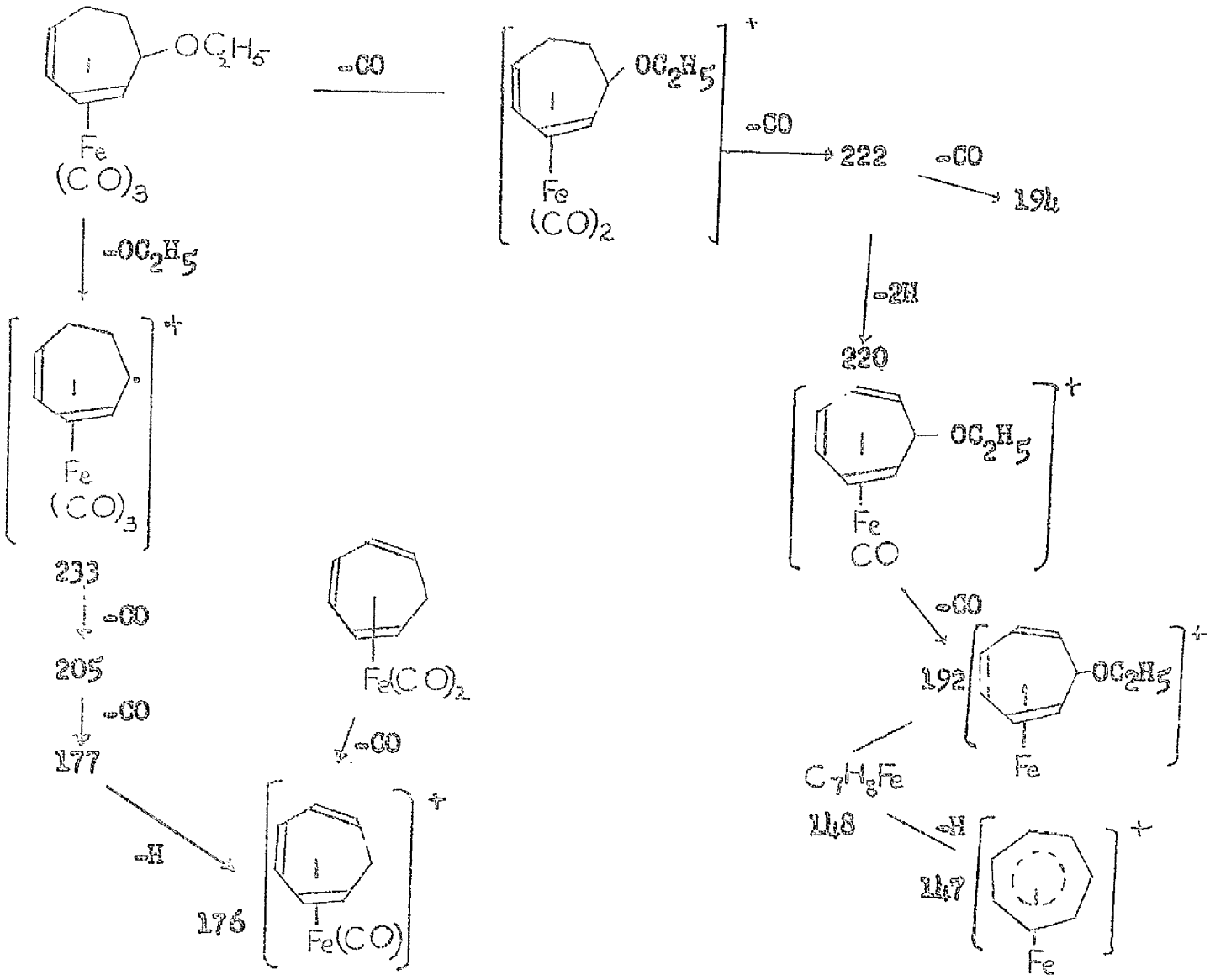
(CIV)

Williamson[65] obtained tricarbonyl cyclohepta-1,3-dieneiron (CIV, R = H) on reduction of cation (LXXXIV) with sodium borohydride or lithium aluminium hydride. The compound (CIV, R = H) exhibits strong absorptions at 2046, 1977 cm^{-1} in metal carbonyl region. Its nuclear magnetic resonance[60] at τ,4.76 has been assigned to the two central diene protons i.e. H_2, H_3. The resonances at τ,6.9 are assigned to the H_1 H_4 protons, while the 4 protons at positions 5 and 7 give rise to the resonance at τ,8.05. The two protons of the CH_2 group at 6 position give rise to a resonance at τ,8.5. All the bands are complex due to spin-spin splitting.

The cation (LXXXIV) reacted with sodium ethoxide and gave orange crystals of tricarbonyl-7-ethoxy-cyclohepta-1,3-dieneiron (CIV, R = OC_2H_5). The structure was established from its analysis and spectral data. Its infra red spectrum shows strong absorptions in metal carbonyl region at 2020, 1988 cm^{-1} (table 4) (see Appendix).

Its nuclear magnetic spectrum displays bands at τ,4.7 (H_2,H_3), 6.7, 8.9 (CH_2, CH_3 of ethoxy group), 6.2 (H_1, H_4, H_7) and 7.6-9.0 (H_5,H_6) (for full details, see Appendix).

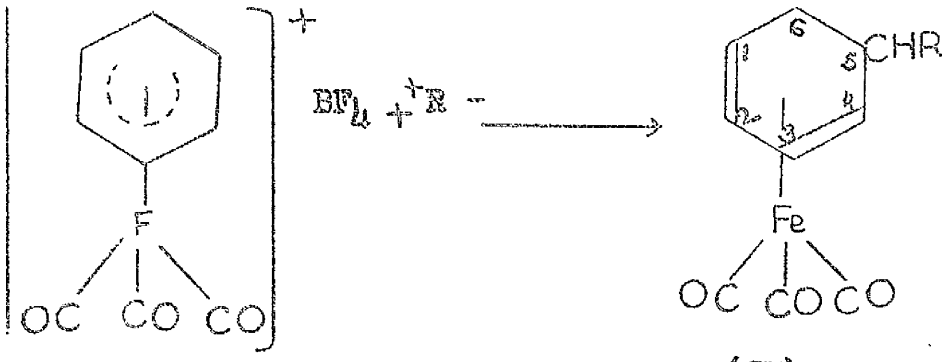
Its structure is further confirmed by its mass spectrum which shows the following cracking pattern



The above pattern clearly establishes that the ethoxy group is attached to a carbon atom adjacent to a diene carbon atom.

The reaction of the compound (CIV, R = OC_2H_5) with trityl fluoroborate resulted in reconversion to complex (LXXXIV).

When treated with sodium methoxide, tricarbonyl cyclohexadienyliron tetrafluoroborate gives a stable yellow oil, tricarbonyl 5-methoxy cyclohexa-1,3-dieneiron (CV, R = OMe) in 58% yield.



(CV)

Its structure (CV, R = OMe) has been established on the basis of analysis and spectral properties.

Its infra red spectrum shows characteristic metal carbonyl absorptions at 2020-1988 cm^{-1} (see table 4) and characteristic ether absorptions at 1075, 1090 cm^{-1}.

The n.m.r. spectrum exhibits one multiplet at τ,4.55 (2) which may be assigned to the aliphatic diene protons H_2,H_3, another multiplet occurs at τ,6.5-7.5 (2) and can be attributed to the protons H_1,H_4. The three protons of the methoxy group give rise to a sharp singlet of intensity 3 at τ,6.85. Two complex bands at τ 8-8.3 and τ 6.25 of relative intensity 2:1 respectively were assigned to resonance of the H_6b,C and H_5a protons respectively (see Appendix).

The methoxyl group can be abstracted by the triphenyl methyl cation to produce the cation (LXXXVII) and triphenylmethyl ether.

To examine the action of the cyanide anion, the cation (LXXXIV) was treated with potassium cyanide in ethanol. Ethanol itself entered

into the reaction producing tricarbonyl 7-ethoxy cycloheptadieneiron along with a residue of prussian blue.

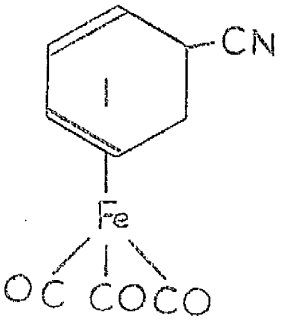
When acetone was used as solvent the reaction gave tricarbonyl 7-cyano-cyclohepta-1,3-dieneiron as a viscous oil. The infra red spectrum of this complex contains a sharp peak of medium intensity at 2237 cm^{-1} characteristic of a $-C\equiv N$ group attached to the cyclic ligand, and metal carbonyl stretching frequencies at 2083 and 2020-1980 cm^{-1}. The complex could not be further purified due to its low stability. Only a small amount could be distilled into a cold fingure and the infra-red spectrum of this oil was identical to that of the product directly obtained.

Tricarbonyl cyclohexadienyliron tetrafluoroborate (LXXXVII) gave tricarbonyl-5-cyanocyclohexa-1,3-diene (CV, R = $\overset{\ominus}{C}N$) by treatment with potassium cyanide in acetone. Its structure (CV, R = $\overset{(-)}{C}N$) was spectrally and analytically established.

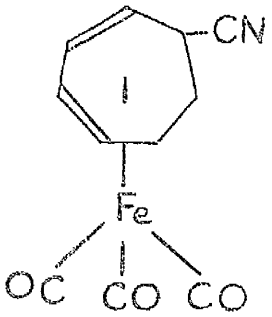
Its infra-red spectrum exhibits $-C\equiv N$ peak attached to the ligand at 2237 cm^{-1} and metal carbonyl absorptions at 2045, 1980 cm^{-1} (see table 4).

The nuclear magnetic resonance spectrum contains peaks at τ, 4.45 (2) which may be attributed to the two central diene protons H_2, H_3. A complex multiplet at τ, 6.8 - 7.1 (3) may be assigned to the H_1, H_4, H_5a protons while another multiplet of intensity 2 arises from the protons Ha, Hc (see Appendix).

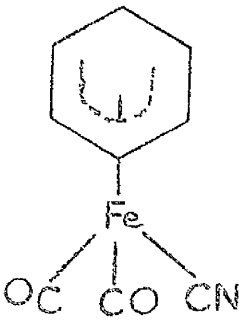
The cyanide anion is abstracted by the triphenyl methyl cation giving the tricarbonyl cyclohexadienyliron cation (LXXXVII)



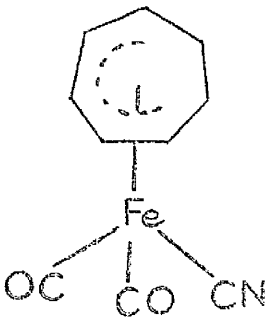
(CVI)



(CVII)

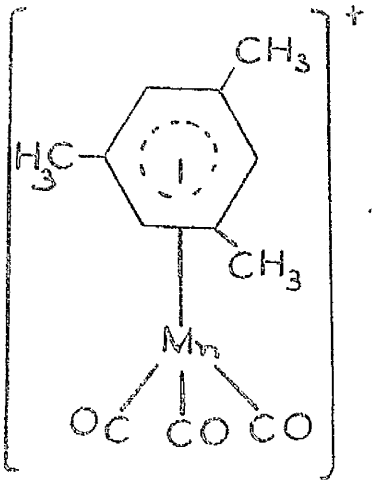


(XCIII)



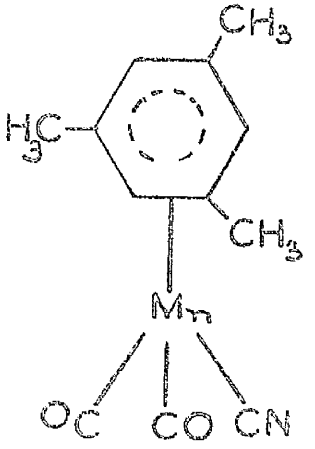
(XCII)

It is significant that in the above mentioned cyanide complexes, the cyanide group attached to iron gives a $-C\equiv N$ stretching mode at 2126 cm^{-1} in the complexes, while the cyanide group attached to the carbocyclic ligand as in the compound (CVI) and (CVII), this mode was shifted towards a higher frequency (i.e. at 2237 cm^{-1}). To confirm the structural assignments tricarbonyl mesitylene-manganese perchlorate (CVIII) was



(CVIII)

$\xrightarrow{\text{NaClO}_4 + \text{KCN}}$



(CIX)

treated with potassium cyanide yielding the complex (CIX)[86]. The infra-red spectrum of the complex (CIX) shows a -C≡N stretching mode at 2128 cm^{-1} (see table 4 in Appendix).

The tricarbonyl cycloheptadienyliron cation (LXXXIV) was treated with the sodium salt of diethyl malonate affording tricarbonyl-7-[di-(ethoxy carbonyl)] methyl-cyclohepta-1,3-dieneiron (CIV, R = $\overset{\frown}{C}H(COOC_2H_5)_2$) as a yellow oil in 62% yield. Its structure (CIV, R = $\overset{\frown}{C}H(COOC_2H_5)_2$) was established from analytical and spectral data.

Its infra-red spectrum shows metal carbonyl absorptions at 2053, 2000, 1996 cm^{-1}, while the n.m.r. spectrum contains complex bands at τ, 4.2-5.0 (H_2,H_3) 5.6-6.3 ($2CH_2$ protons of ethyl group, H_7) 6.8-7.5 (H_1,H_4,H_7), 7.8-8.6 (H_5,H_6) 8.7-9.2 ($2CH_3$ protons of ethyl group). All the bands are complex and unresolved due to spin-spin splitting.

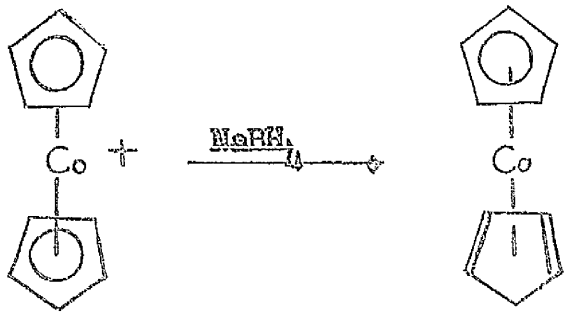
Tricarbonyl-7-[di(ethoxy carbonyl)]methyl-cyclohexadiene (CV, R = $CH(COOC_2H_5)_2$) was prepared analogously from cation (LXXXVII) in 82% yield. The structure was established by analysis and infra-red and n.m.r. spectra.

The infra-red spectra of (CIV, R = $\overset{\frown}{C}H(COOC_2H_5)_2$) and (CV, R = $\overset{\frown}{C}H(COOC_2H_5)_2$ was nearly identical. The characteristic peaks of the metal carbonyl, ester carbonyl and ester -C-O appeared at (2053, 2000, 1996), (1724-1667) and (1176-1053)cm^{-1} respectively. In the n.m.r. spectrum the compound shows resonances at τ,4.7 (H_2,H_3) 5.9 (2 CH_2 protons of ethyl group + H_5a) 6.9 (H_1,H_4), 8.0 (Hb,Hc) and 8.8 (2 CH_3 protons of ethyl groups)(see Appendix). The reactions of

tricarbonyl cyclohexadienyliron cation (LXXXVII) with phenyl lithium at $0^{o}C$ and $-70^{o}C$ in different molecular quantities were tried. These reactions resulted in the formation of tetradicyclohexadienyldiiron and unstable yellowish green oil.

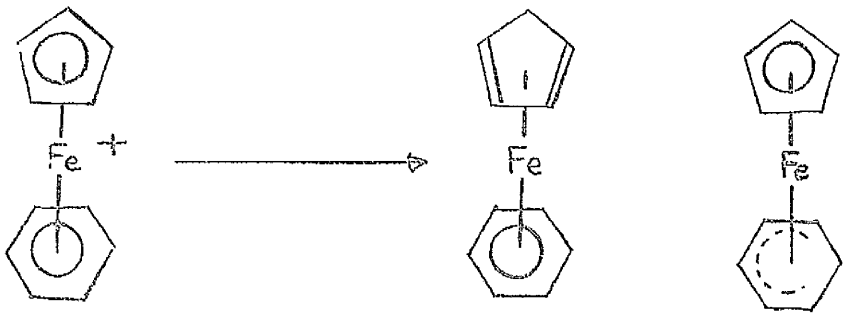
Reduction of diarene cations.

It has been pointed out in the introduction that lithium aluminium hydride or sodium borohydride reduction of the cobalticenium and rhodicenium cations[44] proceed by addition of hydride ion in cyclopentadienyl ligand to form cyclopentadiene complexes, e.g.



Williamson initiated a systematic study of the diarene iron complexes and applied this method of hydride ion addition to prepare corresponding cyclohexadienyliron complexes. This study has been extended by the author.

Wilkinson et al[67] reduced benzene cyclopentadienyliron cation (CX) (as tribromide salt) with lithium aluminium hydride and reported the



(CX) (CXI) (CXII)

formation of (CXI) suggesting that the hydride ion added to cyclopentadienyl ring. Efforts were made to prove this structure on the basis of infra red and n.m.r. spectra (at 40 Mc/s), But the same authors have reformulated the structure of the compound as (CXII) on the basis of further n.m.r. studies[63,67](at 56.4 Mc/s).

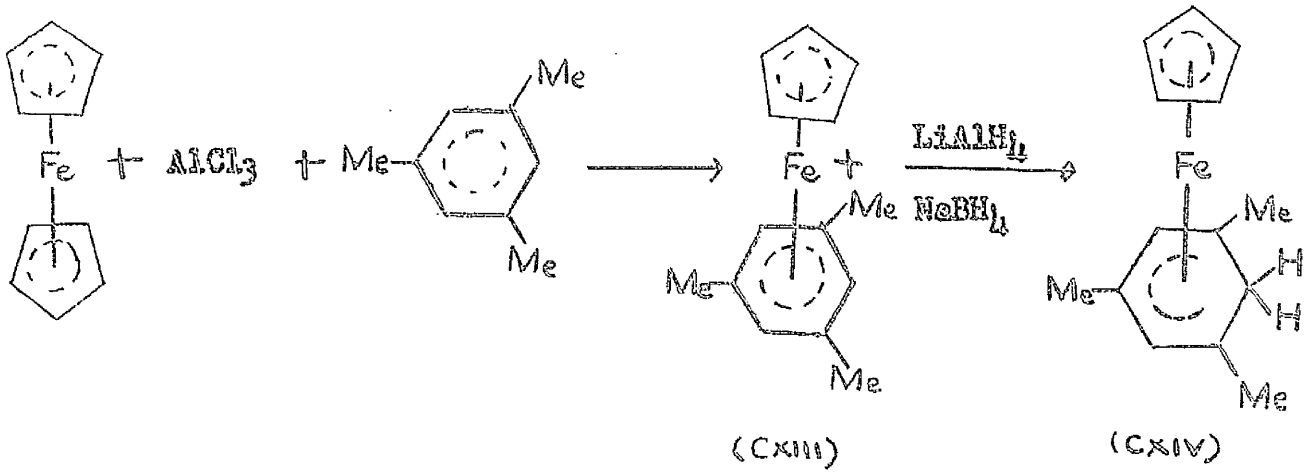
In an effort to add other nucleophiles, the cation (CX) was treated with methoxyl anion but no reaction occurred.

The cation (CX) was further treated with freshly sublimed potassium t-butoxide in tetrahydrofuran, but only starting material was recovered. Other nucleophiles like $-CH(COOC_2H_5)_2$ gave similar results.

However reaction of methyl lithium with the cation (CX) yielded methyl-cyclohexadienyl cyclopentadienyl-iron, an orange oil. Phenyl-cyclohexadienyl cyclopentadienyliron has already been prepared by Wilkinson et al[66] by a similar method. Moreover the cation (CX) reacted with sodium borohydride to give the expected compound (CXII).

To evaluate possible aromaticity of cyclohexadienyl cyclopentadienyl-iron (CXII), Friedel Craft's acetylation was attempted but the reaction resulted in the formation of benzene cyclopentadienyliron cation (CX) and ferrocene.

The cyclopentadienyl mesitylene iron cation (CXIII)[89] was prepared as shown below and was isolated as the tetraphenyl borate and triiodide salts.



(CXIII) (CXIV)

The reduction of the salt (CXIII, $BØ_4$) with lithium aluminium hydride or sodium borohydride yielded 1,3,5-trimethyl-cyclohexadienyl cyclopentadienyliron as red oil.

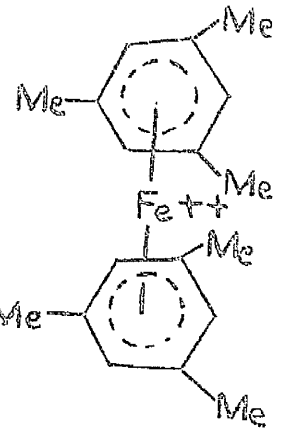
The structure (CXIV) was supported by analysis and infra-red and n.m.r. spectra. The infra-red spectrum of (CXIV) exhibits sharp bands in the C-H stretching region at 3077, 2941, 2857 and 2740 cm^{-1}. It is difficult to resolve the bands due to CH_3 and CH_2 group. However the band at 2941 cm^{-1} may be attributed to methylene group vibrations while the bands at 2857 and 2740 cm^{-1} can be assigned to in-phase and out-of-phase vibrations of two hydrogen atoms of methylene group of cyclohexadienyl ligand[98].

The presence of an exceedingly strong band at 2772 cm^{-1} has been shown the main characteristic of peaks of cyclohexadienyl ligand by Wilkinson et al[67], comparing the infra red spectra of $C_6H_7RuC_6H_8$ and $(\pi\text{-}C_6H_7)_2Ru$.

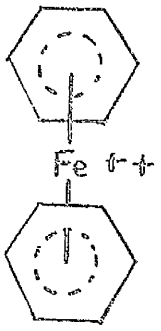
The nuclear magnetic resonance spectrum established that the compound consists of only one isomer. It exhibits a sharp singlet at τ 6.1 of intensity 5 which has been assigned to the 5 protons of cyclopentadienyl group. Two sharp singlets at τ, 7.51 and 8.61 of relative intensity 3:6 have been assigned to the protons of the methyl group at position 4 and two methyl group at positions 1, 5 respectively. Remaining 4 protons show resonances between τ,8-9. The presence of an isomer having a >CHMe group is ruled out due to the lack of splitting of the methyl resonances.

Two methods have been generally applied for the preparation of diarene metal complexes. The first involves reaction of a Grignard reagent with a metal chloride as in the preparation of dibenzene-chromium[90,91]. However a more effective method of wider applicability has been shown to be the direct interaction of an aromatic hydrocarbon with transition metal halides in presence of aluminium chloride as catalyst. Hydrolysis of the reaction mixture affords the cations e.g. $(C_6H_6)_2Ru^{++}$.

Fischer et al[92] reported the preparation of the cations (CXV) and (CXVI). The cation (CXV) was isolated in the form of the tetraphenyl-borate salt but dibenzene iron cation (CXVI) was not isolated since the resulting salt decomposed on addition of water.

a) $FeCl_2 + AlCl_3 + C_6H_3(CH_3)_3$ ⟶  $2AlCl_4^-$

(CXV)

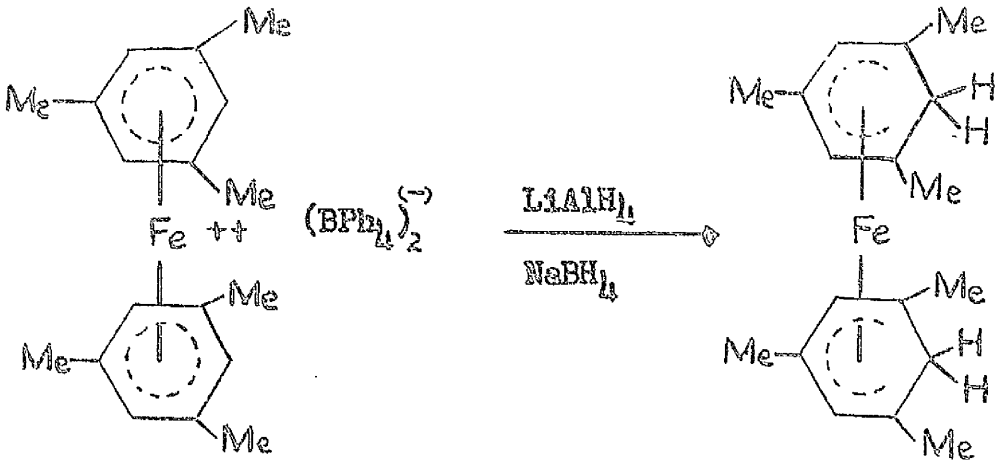
b) $FeCl_2 + AlCl_3 + C_6H_6$ ⟶  $2AlCl_4^-$

(CXVI)

The author undertook the investigation of these cations in an effort to prepare cyclohexadienyliron complexes, a study which had been initiated by Williamson.

A mixture of freshly prepared ferrous chloride and anhydrous aluminium chloride in pure dry mesitylene was refluxed for six hours. The colour of the solution turned reddish brown and on hydrolysis the cation (CXV) was isolated as the tetraphenyl borate.

This salt was treated with lithium aluminium hydride in ethylene glycol dimethyl ether affording yellow crystals of bis (1,3,5 trimethyl cyclohexadienyl) iron



(CXVII)

The structure of the compound was confirmed on the basis of correct analysis and characteristic infra red spectrum.

The complex (CXVII) shows methyl group and methylene group C-H stretching frequencies in the regions 2950-2825 cm^{-1}. Moreover there is no infra red absorptions in the C = C regions but characteristic absorption for a cyclohexadienyl group are present at 1447-1408, 1290, 1075 and 1026 cm^{-1}. Its n.m.r. spectrum could not be obtained due to non availability of the compound.

Regarding the unstable dibenzene-iron cation, Williamson employed lithium aluminium hydride or sodium borohydride for reduction without hydrolysis and obtained an orange crystalline compound.

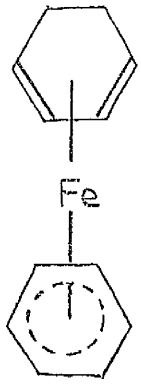
Reduction of dimesitylene-iron cation was carried out by a similar method, i.e. reducing the cation with lithium aluminium hydride without addition of water to isolate the cation. The compound (CXVII)

was obtained and identified by its melting point, mixed melting point and infra-red spectrum.

Dibenzene-iron cation which is unstable in water, was prepared in a similar way. The reddish brown complex (CXVI) was formed and on addition of a suspension of sodium borohydride in 1,2 dimethoxy ethane a vigorous reaction took place and there was obtained an orange compound whose infra red spectrum was identical with that reported by Williamson. However the compound was obtained in too small yield for complete characterization.

The infra red spectrum exhibits peaks in the C-H stretching region at 3030, 2941 and 2857 cm^{-1} which may be assigned to methylene group of cyclohexadienyl ligand and strong absorption at 696, 673 cm^{-1} showing the presence of a benzene nucleus.

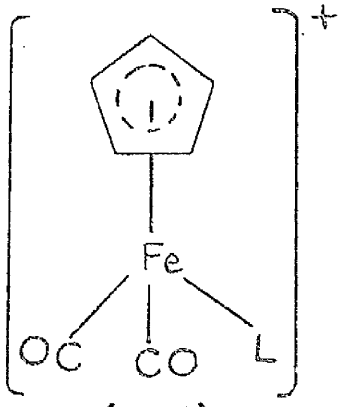
Fischer et al[69] have prepared cyclohexa 1,3-diene, benzene-iron but



(CXVIII)

its infra-red is quite different from that of the product obtained by the author and Williamson (see table 5 in Appendix).

The reaction of π-cyclohexene dicarbonyl cyclopentadienyliron cations with anions

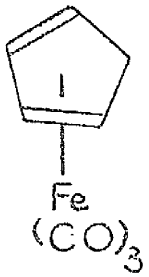


(CXIX)

L = CO, ethylene, propene, cyclohexane butadiene

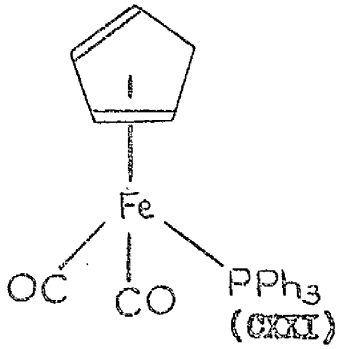
Various cyclopentadienyliron carbonyl complexes e.g. (CXIX) have been mentioned in the introduction where the incorporation of carbonyl or different olefins maintain the inert gas configuration of the iron atom.

It has been shown that a suitable π- cyclopentadienyl metal cation can be reduced by lithium aluminium hydride or sodium borohydride to give cyclopentadiene olefin type complexes e.g. C_5H_5CO C_5H_6. Wilkinson et al[88] prepared cation (CXIX gL = CO), reduced it with sodium borohydride in an unsuccessful effort to prepare tricarbonyl cyclopentadieneiron (CXX)



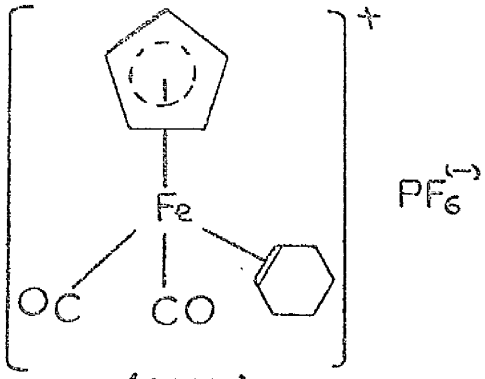
(CXX)

which is an intermediate in the reaction of cyclopentadiene with iron pentacarbonyl to produce dimer $\left[C_5H_5Fe(CO)_2\right]_2$. However the triphenyl phosphine derivative, i.e. $\left[C_5H_5Fe(CO)_2PPh_3\right]Cl$ gave the diene complex (CXXI)



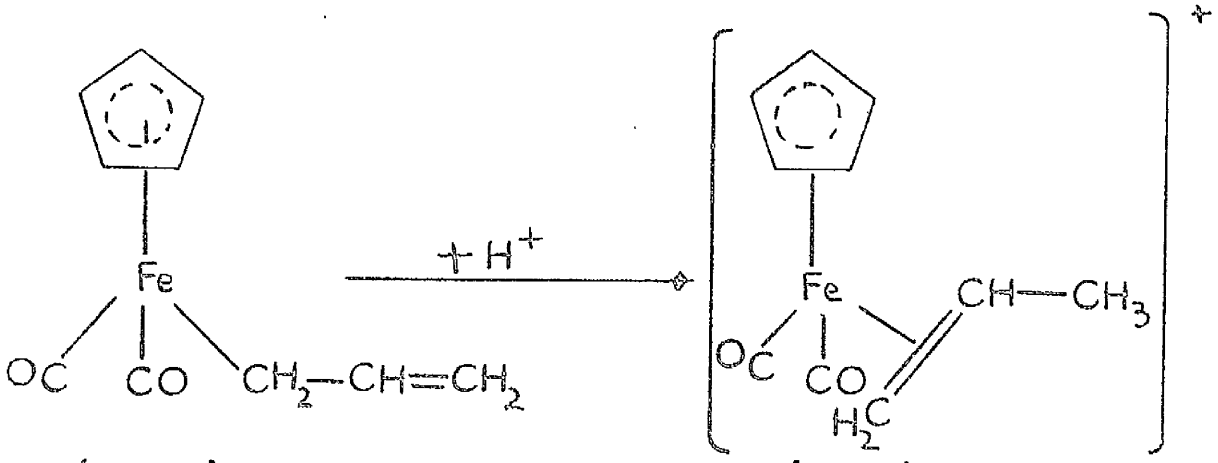
(CXXI)

The interesting interconversion of σ- and π-bonded alkyl and alkenyl substituted cyclopentadienyl cations has been examined by Green and Nagy[94,95,96,97] Cyclohexene dicarbonyl cyclopentadienyliron hexafluorophosphate (CXXII) was selected for such reactions.



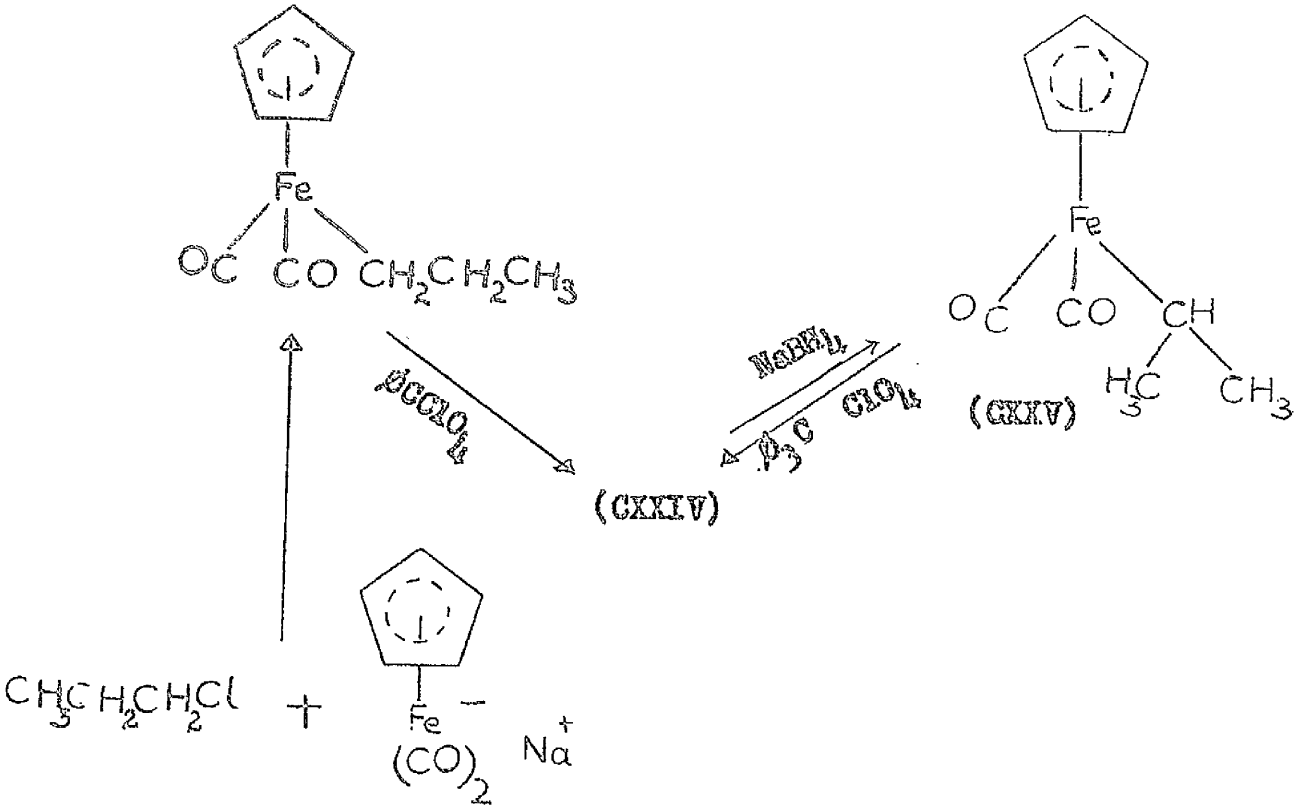
(CXXII)

Nagy and Green[94] protonated the complex (CXXII) during their studies on σ, π alkyl complexes of iron and obtained cation (CXXIV) with a π-bonded propene ligand.



(CXXIII) (CXXIV)

In 1962 the same authors reported a hydride ion abstraction from the σ-bonded alkyl iron complexes[96] and obtained complex (CXXIV). This reaction was found reversible when (CXXIV) was treated with

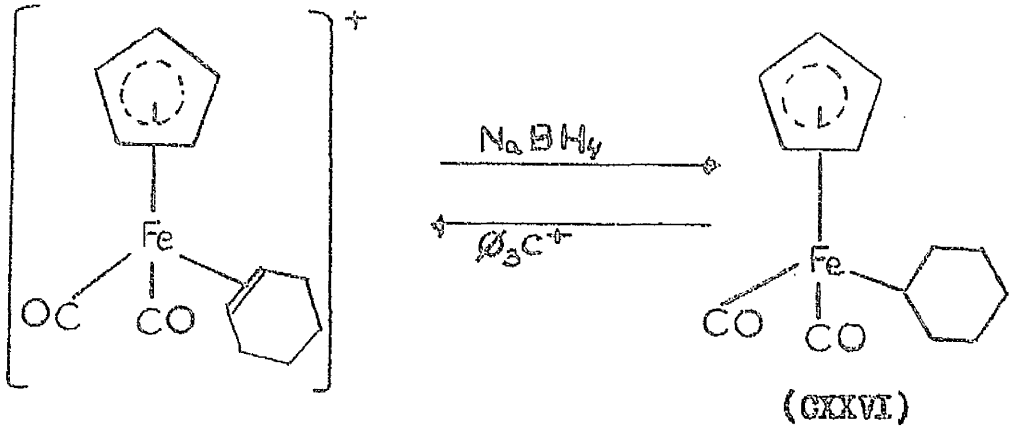


sodium borohydride in tetrahydrofuran complex (CXXV) resulted. The

cation salt prepared from the σ-n.propyl and isopropyl complexes were identical with the π propene cation (CXXIV)

Cyclohexene dicarbonyl cyclopentadienyliron cation (CXXV) reported by Fischer et al[54] was prepared from bromodicarbonyl cyclopentadienyliron, aluminium bromide and cyclohexene. The yield in this case was increased from 38 to 50% by using freshly distilled aluminium bromide. The cation was isolated as hexafluorophosphate salt. The salt could not be prepared on a large scale since the reaction mixture could not be stirred properly due to its high viscosity. The product exhibits absorptions in the C-H stretching region at 3106, 2941 and 2857 cm^{-1} and metal carbonyl bands at 2062, 2016 cm^{-1}, the C=C stretch in the cyclohexene ligand occurs at 1515 cm^{-1}.

The salt on treatment with sodium borohydride in tetrahydrofuran gave cyclohexyl dicarbonyl cyclopentadienyliron (CXXVI) as an amber oil in 50%



(CXXVI)

yield. Though the correct elemental analysis could not be obtained because of the unstable nature, the structure (CXXVI) is confirmed by

the infra red and n.m.r. spectra.

The i.r. spectrum shows C-H stretching modes at 2915, 2840 cm^{-1} and metal carbonyl absorptions at 2000(VS) and 1940 cm^{-1}. The nuclear magnetic resonance spectrumestablished its structure as (CXXVI). It exhibits a singlet at τ, 5.4 (intensity 5) for the cyclopentadienyl protons and broad unresolved band between τ 8.0-9.0 (relative intensity 9) due to the cyclohexyl protons.

The above reaction was found reversible. When compound (CXXVI) was treated with trityl fluoroborate, the cation (CXXII) was isolated as an orange crystalline material. It exhibits metal carbonyl absorption in the infra red at 2062 and 2028 cm^{-1}. (Table No.6)(see appendix).

Reaction of potassium iodide with cation (CXXII) leads to replacement of the cyclohexene group by iodide yielding iododicarbonyl cyclopentadienyliron in 56% yield. The compound was identified from its infra red spectrum.

Cyanide anion was found to attack the cation (CXXII) in an analogous manner and when the reaction was carried out in methanol, cyanodicarbonylcyclopentadienyliron was formed.

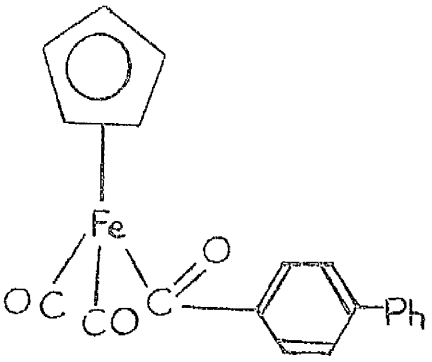
However when (CXXII) was treated with potassium cyanide in a less polar solvent, acetone, two products were formed. The first was a brownish yellow oil which was too unstable to be characterised. Its infra red spectra exhibits metal carbonyl absorption at 2075 and 2012 cm^{-1} and $-C\equiv N$ absorption at 2128 cm^{-1}. This infra-red spectrum is significantly different from that of cyanodicarbonyl cyclopentadienyliron

which was isolated as a second product with it.

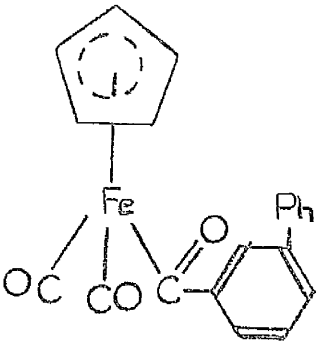
A different reaction occurred when the cation (CXXII) was treated with phenyl-lithium. When a solution of phenyllithium was added to a suspension of equimolar amount of the cation (CXXII) at 0°C, the mixture turned reddish brown. The ether/petrol extract of the reaction product on chromatography gave a red band which yielded a red crystalline compound. This compound could not be characterised due to its small yield, but it showed infra-red maxima at 2933, 2857 cm^{-1} in-C - H stretching region and metal carbonyl absorptions at 2080 and 2000 cm^{-1}.

When the cation (CXXII) was treated with a two-fold excess of phenyl lithium at -70°C, the salt quickly dissolved and the colour of the solution turned yellowish brown. The reaction products were separated chromatographically and the main yellow band eluted by petrol/ether gave an amber oil which could be distilled at 100°C/.005 m.m.

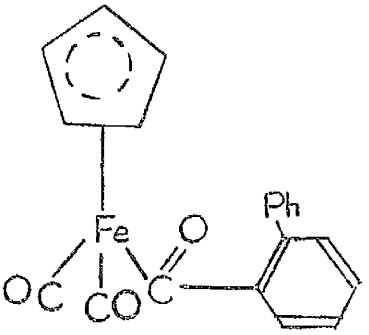
The infra-red spectrum shows the presence of free metal carbonyl groups in the compound by two strong bands at 2020 and 1980-1950 cm^{-1}. Moreover a sharp band of strong intensity at 1655 cm^{-1} suggested the presence of a ketonic carbonyl group probably attached to a metal. The n.m.r. spectrum of the compound shows a multiplet at τ,2.1-3.4 of relative intensity 9 besides a sharp singlet at τ,5.27 (5) for the 5 protons of cyclopentadienyl ligand.



(CXXVII)



(CXXVIII)



(CXXIX)

The structure of this compound remains unestablished although structures of the types (CXXVII, CXXVIII, CXXIX) are in accord with the spectral data and analysis.

E X P E R I M E N T A L

All reactions were carried out under an atmosphere of prepurified nitrogen.

All solvents were rigorously dried according to standard procedure.

Spence's "Grade H" alumina was used for chromatography and was partially deactivated by air exposure to the atmosphere for 6 hours.

Neutralized alumina was prepared by storing "Grade H" alumina under ethyl acetate for more than two days, filtering, washing with methanol then water and finally drying at 160°C for at least 4 hours.

All chromatography columns were protected from light.

All melting points are uncorrected and were determined in sealed, evacuated capillary tubes.

Unless otherwise indicated, all infrared spectra were recorded as potassium chloride discs.

For the sake of convenience the fractions of petroleum ether are referred to as petrol.

N.M.R. spectra were run on a Perkin Elmer 40 m/c Spectrometer using tetramethylsilane as an internal standard.

Ferrous Chloride was prepared by reduction of anhydrous ferric chloride in chlorobenzene[100].

Preparation of trityl perchlorate[101]

Triphenyl carbinol (20 g. 0.077 mole) was taken in a minimum quantity of acetic anhydride. The solution was cooled in acetone/dryice and excess perchloric acid (71%) added dropwise. The temperature of the solution rose sharply and on cooling the dark coloured solution yielded an orange red precipitate of trityl perchlorate (22.6 g. 90%) (Lit. 85%).

Trityl tetrafluoroborate is obtained if fluoroboric acid (40%) is used instead of perchloric acid[101].

Tricarbonyl-π-cycloheptatrieneiron[70]

Freshly distilled cycloheptatriene (70 ml) and iron pentacarbonyl (30 cc. 43.8 g) were refluxed for 15 hours at 135°C. Unchanged starting materials were removed by vacuum distillation in the cold. Tricarbonyl cycloheptatrieneiron was distilled at ~80-85°C/2 mm. yield, 19.18 g. 45%.

Preparation of tricarbonyl π-cycloheptadienyliron fluoroborate[70]

A solution of hydrofluoroboric acid (40%, 2 g) in propionic anhydride (5 ml) was added to a solution of tricarbonyl cycloheptatrieneiron (3.3 g. 0.043 mol) in propionic anhydride (4 ml). After shaking the solution in ice cooled water a yellow precipitate settled. It changed colour from light yellow to brown on standing. After filtering, the precipitate was washed with petrol (b.p. 40-60°) affording bright yellow crystals (4.02 g. 87.4%) of tricarbonyl π-cycloheptadienyliron tetrafluoroborate. Colour darkens without melting above 150° (Lit. colour darkens at 160°C).

Tricarbonyl π-cyclohexadieneiron[6]

Freshly distilled cyclohexa-1,3,diene (12 g) (prepared by treatment of 1,2-dibromocyclohexane with quinoline, purified by treatment with H_2SO_4(dil) dried and distilled over sodium) and iron pentacarbonyl (20 g) were heated under carbon dioxide in an autoclave for 24 hours at 130°-135°C. A reddish yellow oil without any solid material was obtained. Unchanged iron pentacarbonyl was removed by vacuum distillation in cold. Tricarbonyl cyclohexadieneiron was obtained as yellow oil with camphoraceous smell, b.p. 96/12 mm, yield 6.5 g.

Tricarbonyl 1,3 cyclo~~clo~~hexadiene is also obtained by 1,4 cyclohexadiene (prepared by reduction of pure benzene by Birch reduction).

Tricarbonyl cyclohexadienyliron tetrafluoroborate[64]

A solution of tricarbonyl cyclohexadiene (5.5 g. 0.025 mole) in methylene chloride (10 ml) was treated with a solution of trityl fluoroborate (8.0 g. 0.058 mole) in methylene chloride (25 ml). The yellow solution changed to yellowish green and after a few minutes a yellow precipitate settled. After filtering, the precipitate was washed with methylene chloride affording yellow crystals (6 g. 84%) of tricarbonyl cyclohexadienyliron tetrafluoroborate m.p. 193°(decomp) (Lit decomp at 190°).

Iododicarbonyl π-cycloheptadienyliron[70]

Tricarbonyl π-cycloheptadienyliron tetrafluoroborate (6.4 g. 0.02 mole) was dissolved in acetone (250 ml) and potassium iodide (3.47 g. 0.0021 mole) was added to the solution. The yellow solution which turned reddish brown

with the evolution of carbon monoxide was stirred for three hours at 30°C. After evaporation to dryness the residue was extracted with benzene and the solution filtered through a short column of alumina. Benzene was evaporated under vacuum and iododicarbonyl π-cycloheptadienyliron was crystallized from chloroform/petrol (b.p. 60°-80°) in maroon crystals (3.4 g. 51%) m.p. 90-92° (Lit 86-89°).

Iododicarbonyl π-cyclohexadienyliron

Freshly prepared and thoroughly dried tricarbonyl π-cyclohexadienyliron perchlorate (1.84 g. 0.00581 mole) was dissolved in acetone (100 ml). Potassium iodide (0.90 g. 0.0054 mole) was added and the mixture stirred for three hours at 30°C. The solvent was removed under vacuum. The residue was extracted with chloroform (50 ml x 4) and filtered through a short column of alumina. The reddish brown solution on evaporation to small bulk and on addition of petrol (b.p. 60-80°) yielded reddish brown crystals of iododicarbonyl π-cyclohexadienyliron (0.86 g. 47% yield) m.p. 95-96°.

Analysis found C, 30.1; H, 2.25; I, 40.5

$C_8H_7FeO_2I$ requires C, 30.1; H, 2.5 ; I, 39.8%

Tetracarbonyl-π-dicycloheptadienyldiiron

To a solution of freshly prepared iododicarbonyl-π-cycloheptadienyliron (0.83 g. 0.0025 mole) in tetrahydrofuran (25 ml), sodium amalgum (1%, 6 g. 0.0026 g. atom) was added. The mixture was stirred over one hour. The reddish brown solution turned red with turbidity. After removing solvent under vacuum the red residue was extracted with methylene chloride (200 ml x 2).

The solution was kept under nitrogen during extraction and filtration. Concentration of solution and addition of petrol (b.p.40-60°) yielded red shining crystals of tetracarbonyl di-π-cycloheptadienyldiiron (0.21 g. 41%) m.p. 198°C.

Analysis found C, 52.7, H, 4.5; O, 15.8

$C_{18}H_{18}Fe_2O_4$ requires C, 52.7, H, 4.25; O, 15.6%

Tetracarbonyl π-cycloheptadienyl π-cyclopentadienyldiiron

A solution of sodium cyclopentadienide (0.01 mole) prepared by adding freshly distilled cyclopentadiene (2 ml) to sodium (1.23 g. 0.01 g.atom) in tetrahydrofuran (50 ml). Freshly prepared iodocarbonyl π-cycloheptadienyliron (3.32 g. 0.01 mole) was added and the mixture was stirred for 1 hour at room temperature. The solution turned from pinkish red to reddish brown. The solvent was evaporated under vacuum and the residue was extracted with petrol (b.p.60-80°) and then with benzene. The extract was concentrated and chromatographed on alumina (6 hours deactivated).

(a) A yellow band was eluted with petrol (b.p.60-80°). This yielded a yellow crystalline solid (32 mg.) which decomposed to a brown mass within a few hours even on preserving it under nitrogen. It could not be sublimed under high vacuum.

(b) An orange red band was separated by petrol (b.p.60-80°)/benzene (1:1). On evaporation it afforded oily material in insufficient quantity for identification.

(c) A main purple band from which tetracarbonyl π-cycloheptadienyl π-cyclopentadienyldiiron was obtained (44 mg.). The reddish brown crystalline

compound was further crystallized from methylene chloride/petrol (b.p. 40-60°) m.p. 168-170°.

Analysis found C, 50.3; 50.4; H, 3.7, 3.6

$C_{16}H_{14}Fe_2O_4$ requires C, 50.3; H, 3.7%

Tetracarbonyl-di-cyclohexadienyldiiron

Freshly prepared iodocarbonyl π-cyclohexadienyliron (0.1 g. 0.0026 mole) was dissolved in tetrahydrofuran. Sodium amalgum (1%, 0.84 g. 0.00037 g.atom) was added and the mixture stirred for 30 minutes. The brown solution turned red and became turbid after 15 minutes. If the solution is stirred more than 30 minutes the reaction mixture is decomposed. The solvent was quickly removed in vacuo. The red residue was extracted with methylene chloride (100 ml x 2). The solution was kept under nitrogen during extraction and filtration. A red solution on concentration under vacuum and on addition of petrol (b.p. 40-60°) yielded pinkish red crystals of tetracarbonyl-di-cyclohexadienyldiiron (22 mg, 34%). It darkens at 160-162° without melting.

Tetracarbonyl π-cyclohexadienyl-π-cyclopentadienyldiiron

A solution of sodium cyclopentadienide (0.005 mole) was prepared by adding freshly distilled cyclopentadiene (0.5 ml) to sodium (0.12 g. 0.005 g.atom) in tetrahydrofuran. Freshly prepared iododicarbonyl-π-cyclohexadienyliron (1.58 g. 0.005 mole) was added and the mixture stirred for one hour. The solution turned reddish brown from pinkish red. The solvent was removed under vacuum and the residue was extracted with petrol

(b.p.60-80°) and then with benzene. The concentrated extract was chromatographed on alumina (neutral, 6 hour deactivated).

A yellow semi solid substance (0.012 g.) was eluted with petrol (b.p. 60-80°) and preserved under nitrogen; but it decomposed after a few hours.

Then a reddish brown band on elution with petrol (b.p. 60-80°)/ benzene (1:1) afforded a crystalline solid. The product starts decomposing while removing the solvent under vacuum.

Cyanodicarbonyl π-cycloheptadienyliron

A solution of freshly prepared iododicarbonyl π-cycloheptadienyliron (1.66 g. 0.005 mole) in acetone (50 ml) was mixed with a solution of potassium cyanide (0.325 g. 0.005 mole) in methanol (20 ml) and stirred for three hours at room temperature. The brown colour changed to yellow. The solvent was removed under vacuum, and the residue was extracted with chloroform and filtered through a small column of alumina. Evaporation to small bulk and addition of petrol (b.p.60-80°C) yielded pale orange crystals of cyanodicarbonyl-π-cycloheptadienyliron (0.68 g. 68%) m.p. 75-76°(decomp).

Analysis found C, 51.9, H, 4.4; O, 14.0, N, 6.3

$C_{10}H_5FeNO_2$ requires C, 52.0, H, 3.9; O, 13.85; N, 6.1%

Cyanodicarbonyl π-cyclohexadienyliron

Freshly prepared iododicarbonyl π- cyclohexadienyliron (0.636 g. 0.002 mole) was dissolved in dried methanol. Potassium cyanide (0.13 g. 0.002 mole) was added ~~and~~ the mixture and was stirred at room temperature.

A whitish yellow precipitate settled down and the solvent was evaporated under vacuum and the product was extracted with chloroform.

A yellow crystalline product, cyanodicarbonyl π-cyclohexadienyliron (0.082 g. 22%), m.p. 90-91° was obtained. The compound decomposed during crystallization.

Tricarbonyl-7-ethoxy cyclohepta-1,3-dieneiron

To a solution of sodium ethoxide (from sodium (0.07 g. 0.0033 mole) in ethanol (5 ml.)) tricarbonyl-π-cycloheptadienyliron tetrafluoroborate (1.06 g. 0.003 mol) was added. The mixture was stirred for one hour. The solvent was removed in vacuo and the residue was extracted with petrol (b.p. 60-80°). The extract was evaporated to dryness giving a viscous oil. It afforded orange crystals of tricarbonyl-7-ethoxy-cyclohepta-1,3-dieneiron on sublimation at 50°/0.005 mm. m.p. 62-65° (0.66 g. 61%) It can also be crystallized from petrol (b.p. 60-80°).

Analysis found C, 51.8; H, 5.2; O, 23.2

$C_{10}H_{11}FeO_4$ requires C, 51.8; H, 5.1; O, 23.0%

Reaction of triphenyl methyl fluoroborate with tricarbonyl-7-ethoxy-cyclohepta-1,3-dieneiron.

A solution of freshly prepared tritylfluoroborate (0.33 g. 0.001 g.) in dry methylene chloride (5 ml.) was added to a solution of tricarbonyl-7-ethoxy-cyclohepta-1,3-dieneiron (0.3g. 0.001 mole) in methylene chloride (2 ml.). After a few minutes, a yellow crystalline precipitate settled. It was filtered off and identified as tricarbonyl-π-cycloheptadienyliron tetrafluoroborate (0.17 g. 84%) on the basis of infrared comparison with an authentic sample.

Attempted reaction of tricarbonyl-π-cyclohepdienyliron tetrafluoroborate with potassium cyanide in ethanol.

Tricarbonyl cycloheptadienyliron tetrafluoroborate (2 g. 0.00625 mol) solution in carefully dried ethanol (400 ml.) was treated with potassium cyanide (0.4 g. 0.00871 mole) and stirred overnight. The colour of the solution changed from yellow to pale yellow and a blue precipitate separated out. After removing the solvent, the residue was extracted with petrol (b.p. 60-80°). A viscous oil on sublimation at 76°/0.005 mm afforded orange crystals (0.90 g.) identified as tricarbonyl-7-ethoxy-cyclohepta-1,3-diene m.p. 62° by its melting point, and by infrared spectral comparison with an authentic sample.

Tricarbonyl-7-cyano-cycloheptadieneiron.

Tricarbonyl-π-cyclohentadienyliron tetrafluoroborate (2.4 g. 0.007501 mole) was dissolved in acetone (250 ml). Potassium cyanide (0.435 g. 0.007 mole) was added and the mixture was stirred 12 hrs. The colour of the solution changed from yellow to dirty pale yellow. After removing the solvent under vacuum, the residue was extracted with petrol (b.p. 40-60°). The extract was concentrated to small bulk and chromatographed on neutral alumina (3 hrs. deactivated).

A yellow band eluted by petrol (b.p. 40-60°) afforded an orange oil (0.02 g.) which could not be identified due to its instability.

The second band on elution with benzene yielded tricarbonyl-7-cyano-cyclohepta-1,3-dieneiron (0.74 g. 48%) as a viscous oil. The product

could not be purified as the oil decomposed before distillation. Only a small amount could be sublimed as a semi solid mass

Reaction of tritylfluoroborate with tricarbonyl-7-cyano-1-cyclohepta-1,3-dieneiron

A solution of tritylfluoroborate (0.066 g. 0.0002 mole) in methylene chloride (2 ml) was treated with tricarbonyl-7-cyano-π-cyclohepta-1,3-dieneiron (0.05 g. 0.0002 mole) in methylene chloride (5 ml). A yellow precipitate was filtered off and washed with methylene chloride. It was identified as tricarbonyl-π-cycloheptadienyliron tetrafluoroborate by comparison of its infrared spectrum with that of an authentic sample.

Tricarbonyl-7-di(ethoxycarbonyl)methyl cycloheptadieneiron

Diethyl malonate (1.6 g. 0.01 mol) was added to a solution of sodium ethoxide prepared from sodium (0.23 g. 0.01 mol) in ethanol (5 ml) and the mixture was stirred for 30 minutes. Tricarbonyl-π-cyclohepta-dienyliron tetrafluoroborate (3.2 g. 0.01 mol) was added. The mixture was stirred for 15 minutes. The solvent was removed in vacuo. The yellow residue was extracted with petrol (b.p. 60-80°) and benzene. The extract was concentrated to small bulk and was chromatographed on neutral alumina (3 hrs. deactivated). A yellow band, eluted with petrol (b.p. 60-80°)/benzene, afforded a yellow oil (3.07 g. 62%) (distilled at 70°/0.005 mm) of

tricarbonyl-7-di(ethoxycarbonyl)methyl cycloheptadieneiron.

Analysis found	C,	52.5%	H,	5.2%	O, 28.5
$C_{17}H_{19}O_7Fe$ requires	C,	52.2%	H,	4.9%	O, 28.6 %

Attempted reaction of triphenyl methyl fluoroborate with tricarbonyl-7-di(ethoxycarbonyl)methyl cyclohepta-1,3-dieneiron.

A solution of freshly prepared tritylfluoroborate (0.33 gm. 0.01 mol) in methylene chloride (5 ml) was added to a solution of tricarbonyl-7-di(ethoxycarbonyl)methyl cyclohepta-1,3-diene (0.4 g. 0.01 mol) in methylene chloride. No precipitate was obtained. The solvent was removed under vacuum and the residue was extracted with petrol (b.p. 60-80°C). Unreacted tricarbonyl-7-di(ethoxycarbonyl)methyl cyclohepta-1,3-dieneiron was recovered and identified by infrared spectral comparison with an authentic sample.

Attempted reaction of phenyllithium with tricarbonyl cyclohexadienyliron tetrafluoroborate

(a) Lithium metal (0.07 g. 0.01 mole) cut into small peices in dry ether (25 ml) was added to a solution of bromobenzene (1.57 g. 0.01 mole) in dry ether (20 ml) at such a rate that a steady refluxing is maintained. After two hours, when the reaction is completed the solution was filtered through glass wool

Tricarbonyl cyclohexadienyliron tetrafluoroborate (1 g. 0.003 mole) was added to the solution of phenyllithium in two fold excess at 0°C. The salt went quickly into solution. The colour of the solution changed yellowish red from orange. It was stirred for 15 minutes to complete the reaction. The solution was washed with water. The red ether layer was dried (anhydrous $CaCl_2$). The solution started to decompose. The solution was filtered and the solvent was removed under vacuum. The residue was extracted with petrol (b.p. 40-60°) and then methylene chloride. The yellow extract started to decompose while removing the solvent under vacuum. It was chromatographed on neutral alumina.

A green band was eluted with petrol (b.p. 40-60°). The product was found very unstable.

A yellow oil (0.023 g.) was eluted by petrol (b.p. 40-60°)/benzene. It did not show phenyl group peaks in infrared spectrum.

Another fraction containing yellow oil (0.004 g.) was eluted with ether.

Both benzene and ether fraction, decomposed partially into greenish white mass, when treated with triphenylmethyl fluoroborate in methylene chloride, gave a yellow precipitate identified as tricarbonyl cyclohexadienyl-iron tetrafluoroborate by infrared spectral comparison with an authentic sample. The methylene chloride red extract gave shining red crystals (0.04 g.) of tetracarbonyl dicyclohexadienyldiiron identified by infrared spectral comparison with an authentic sample.

(b) Phenyllithium [prepared by lithium (0.04 g. 0.005 mole) with bromobenzene (0.78g. 0.005 mole in ether (50 ml)] was added to a suspension of tricarbonyl cyclohexadienyliron tetrafluoroborate (0.5 g. 0.0016 mole in ether at room temperature. The salt dissolved in the solution after 15 minutes. Dry ice was added to destroy the phenyl lithium. The solution was washed with water and extracted with petrol (b.p. 40-60°) and then with methylene chloride. The methylene chloride extract on removing the solvent afforded shining red crystals identified as tetracarbonyl dicyclohexadienyldiiron by infrared spectral comparison with an authentic sample.

The red petrol extract was chromatographed on neutral alumina.

(a) A greenish yellow product (0.09 g.) eluted by petrol was decomposed in greenish white mass.

(b) A yellow oil (0.14 g.) was eluted by benzene. It did not show phenyl peaks in the infrared and afforded tricarbonyl cyclohexadienyliron tetrafluoroborate on treatment with triphenyl methyl fluoroborate in methylene chloride.

Tricarbonyl-π-5-methoxy cyclohexa-1,3-dieneiron.

Tricarbonyl-π-cyclohexadienyliron tetrafluoroborate (1 g. 0.031 mole) was added to a solution of sodium methoxide prepared from sodium (0.17 g. 0.0074 g.atom) in absolute methanol (5 ml) and the mixture was stirred overnight. The salt went quickly into solution. The solvent was removed in vacuo and a yellow oily residue was extracted with petrol b.p. (40-60°). Evaporation of solvent under vacuum gave an oil with

camphoraceous odour. The oil was distilled at 40°C/0.005 mm yielding tricarbonyl-5-methoxy-cyclohexa-1,3-dieneiron (0.43 g. 53%)

Analysis found C, 48.1% H, 4.1% O, 25.8

, 48.2 4.0

$C_{10}H_{10}FeO$ requires C, 48.0%; H, 4.0%; O, 25.6%

I.R. ν_{max} 1988 - 2020 cm^{-1}, 1075 - 1090 cm^{-1}

Reaction of triphenylmethylfluoroborate with tricarbonyl-5- methoxy-cyclohexa-1,3-dieneiron

A solution of freshly prepared triphenyl methyl fluoroborate (0.33 g. 0.001 mole) in dry methylene chloride (5 ml) was added to a solution of tricarbonyl-5-methoxy-π-cyclohexa-1,3-dieneiron (0.25 g. 0.001 mole) in methylene chloride (2 ml). A yellow crystalline product settled in a few minutes. It was washed with methylene chloride. It was identified as tricarbonyl-cyclohexadienyliron tetrafluoroborate (0.28 g. 92%) by infrared spectral comparison with an authentic sample.

Attempted reaction of potassium cyanide with tricarbonyl-π-cyclohexa-dienyl-iron tetrafluoroborate in methanol

Tricarbonyl-π-cyclohexadienyliron tetrafluoroborate (1.02 g. 0.0033 mole) in methanol (200 ml) was treated with potassium cyanide (0.21 g. 0.003 mole). The mixture was stirred for 6 hrs at room temperature. The solution turned pale yellow with a blue turbidity. The solvent was removed under vacuum. The oily residue was extracted

with petrol (b.p. 40-60°). The yellow oil, obtained after removing the solvent was identified as tricarbonyl-5-methoxy-cyclohexa-1,3-diene by its camphoraceous smell and by infrared spectral comparison with an authentic sample. Yield 0.27 g. 41%.

Tricarbonyl-π-5-cyanocyclohexa-1,3-dieneiron

Tricarbonyl-π-cyclohexadienyliron tetrafluoroborate (1.02 g. 0.0034 mole) was dissolved in acetone (200 ml). Dry potassium cyanide (0.3 g. 0.0046 mole) was added with acetone (100 ml). The mixture was stirred for 18 hrs. The yellow colour faded with production of a green precipitate, which was filtered off. The solvent was removed under vacuum and the residue was extracted with petrol (b.p. 40-60°). The yellow extract gave a viscous yellow oil. This oil was sublimed at 50°/0.005 mm yielding pale yellow crystals of tricarbonyl-5-cyano-π-cyclohexa-1,3-dieneiron (0.48 g. 58.9%) m.p. 95°.

Analysis found C, 48.7% H 3.1% O, 19.7% N, 5.7

$C_{10}H_7O_3NFe$ requires C, 49.0%, H 2.9% O, 19.6% N, 5.7%

I.R. ν max. 2045, 1980, 2237 cm^{-1}.

Reaction of triphenyl methyl fluoroborate with tricarbonyl-5-cyano-cyclohexa-1,3-dieneiron.

A solution of freshly prepared triphenyl methyl fluoroborate (0.2 g. 0.0006 mole) in dry methylene chloride (5 ml) was added to a solution of tricarbonyl-5-cyano-π-cyclohexa-1,3-dieneiron (0.1 g. 0.00041 mole) in methylene chloride (5 ml). A yellow crystalline product settled down

in a few minutes. It was washed with methylene chloride and identified as tricarbonyl-π-cyclohexadienyliron tetrafluoroborate by infrared spectral comparison with an authentic sample.

Tricarbonyl-5-di(ethoxycarbonyl)methyl cyclohexa-1,3-dieneiron

Diethyl malonate (0.53 g. 0.0033 mole) was added to sodium ethoxide prepared from sodium (0.07 g. 0.003 mole) in absolute ethanol (10 ml) and stirred for 15 minutes. Tricarbonyl-π-cyclohexadienyliron tetrafluoroborate (1.02 g. 0.0033 mol) was added. The salt was dissolved quickly and after a few minutes a whitish yellow precipitate settled. The mixture was stirred for 30 minutes. The solvent was removed under vacuum and the oily residue was extracted with petrol (b.p. 40-60°) and then benzene. Evaporation of solvent yielded a yellow oil which was chromatographed on neutral alumina (deactivated for 3 hrs). A yellow band was eluted by petrol (b.p. 60-80°)/benzene (1:1). It afforded tricarbonyl-5-di(ethoxycarbonyl) methyl-π-cyclohexa-1,3-dieneiron (.96g. 82%) as a yellow oil distilled at 60°/0.001 mm.

Analysis found C, 50.7; H, 4.9. O 29.8

$C_{16}H_{18}O_7Fe$ requires C, 50.8; H, 4.8; O 29.6%

I.R. ν max. 2066, 1961 cm^{-1}, 1724-1667, 1176-1053 cm^{-1}.

Attempted reaction of triphenyl methyl fluoroborate with tricarbonyl-5-di(ethoxycarbonyl)methyl-π-cyclohexa-1,3-dieneiron.

Tritylfluoroborate (0.11g. 0.003 mole) in methylene chloride (5 ml.)

was treated with a solution of tricarbonyl-5-di(ethoxycarbonyl)methyl cyclo-1,3-dieneiron (0.1g. 0.0034 mole) in methylene chloride (5 ml). No precipitate was obtained. After 10 minutes the solvent was evaporated and the residue was extracted with petrol (b.p. 60-80°). The starting material was recovered.

Preparation of mesitylenecyclopentadienyliron tetraphenylborate[89]

A mixture of ferrocene (5 g. 0.025 mole) anhydrous aluminium trichloride (7.1 g. 0.0535 mole) and aluminium powder (0.7 g. 0.025 g.atom) and mesitylene (200 ml) was refluxed for four hrs. The colour of the mixture changed from orange to red brown. Water (200 ml) was added carefully after cooling the reaction mixture and stirred vigorously. The water layer was separated and washed with petrol (b.p. 60-80°) and treated with a solution of sodium tetraphenylborate in excess. Mesitylenecyclopentadienyliron tetraphenylborate (7.1 g. 54%) was isolated as red crystals 257-259°C (Lit.258°C). It was purified by recrystallization from acetone/ether.

Preparation of Tris cyclopentadienyliron triiodide[89]

A mixture of ferrocene (3 g. 0.0161 mole) aluminium trichloride (anhydrous)(7.2 g. 0.0161 mol) and aluminium powder (0.43 g. 0.0159 mole) and xylenes (200 ml) was refluxed for four hours. Water (200 ml) was added carefully after cooling the solution. The yellow water layer was washed with petrol (b.p. 60-80°) and a solution of potassium iodide and iodine (5:1) in water was added. The orange precipitate of mesitylene cyclopentadienyliron triiodide (2.0 g.) was dried and recrystallized from acetone/ether (m.p. 226-229°).

Trimethyl-1,3,5-cyclohexadienyl-π-cyclopentadienyliron

(a) Using Lithium aluminium hydride

To mesitylene cyclopentadienyliron tetraphenylborate (5 g. 0.0089 mol)

in diglyme glyme dimethyl ether (20 ml) added. Ammonium [illegible] was added in small portion and the mixture stirred for one hr. The reaction started spontaneously and the colour of the solution turned red. Methanol (20 ml) was carefully added and then water (100 ml). After addition of petrol (b.p. 60-80°)(50 ml), the organic layer was washed with water (50x2), dried (anhydrous $CaCl_2$), concentrated and chromatographed on neutral alumina. The only red band eluted with petrol (b.p. 60-80°C) afforded 1,2,5-trimethyl-cyclohexadienyl-π-cyclopentadienyliron (0.83 g.) as a red oil purified by distillation at 50°/0.005 mm.

Analysis found C, 69.5%; H, 7.7%

$C_{14}H_{18}Fe$ requires C, 69.5%; H, 7.5%

I.R. (liq.) [illegible] 2914, 2860 [illegible] 1450 [illegible] 1380, 1011 cm⁻¹

(b) From cyclohexadienyl hydride

1-methyl-cyclohexadienyl-π-cyclopentadienyliron (1 g. 0.0042 mole) in diglyme glycol dimethyl ether (50 ml) was treated with sodium borohydride (5 g.) in small portions. The reaction mixture was stirred vigorously for two hours. Water (100 ml) was added carefully. After addition of petrol (100 ml b.p. 60-80°) the organic layer was washed with water, dried (anhydrous $CaCl_2$) and concentrated to small bulk. It was chromatographed on neutral alumina. A red band on elution with petrol (b.p. 60-80°) yielded π-cyclohexadienyliron (0.432 g. 36.8%) distilled at 50°/0.005 mm

Identified by comparison of infrared spectrum with that of sample prepared by method (a).

Attempted reaction of trityl fluoroborate with 1,3,5-trimethyl-cyclohexadienyl cyclopentadienyliron

Triphenyl methyl fluoroborate (0.4 g. 0.00121 mole) was dissolved in methylene chloride (10 ml). The solution was treated with a solution of trimethyl-1,3,5-cyclohexadienyl cyclopentadienyliron (0.2 g. 0.000825 mole) in methylene chloride (2 ml). An orange precipitate settled after a few minutes. The mesitylene cyclopentadienyliron tetrafluoroborate (0.22 g. 44.4%) was crystallized with acetone/ether m.p. 160°C(decomp) and identified by its infrared spectrum.

Bis-(η-1,3,5-trimethyl cyclohexadienyl)iron.

(a) Using lithium aluminium hydride

Dimesitylene-iron bis tetraphenylborate (5 g. 0.00515 mole) in ethylene glycol dimethyl ether (50 ml) was treated with lithium aluminium hydride (2 g.) in small portions. The mixture was stirred for three hrs and petrol (b.p. 40-60°) was added. Then the mixture was treated with methanol (10 ml) and then water (100 ml). The organic layer was separated and dried (anhydrous $CaCl_2$). On removing the solvent in vacuo a yellow residue was obtained. It was dissolved in petrol (b.p. 40-60°) and chromatographed on alumina. A yellow band on elution with petrol (b.p. 40-60°) gave yellow crystals of bis (trimethyl-1,3,5-cyclohexadienyl)iron (0.72 g. 45.2%) m.p. 125-127°.

Analysis found C, 72.3%; H, 8.5

$C_{18}H_{26}Fe$ requires C, 72.5%; H, 8.8%

I.R.) max. 2941, 2858, 1515, 1447, 1406, 1370, 1365, 1290, 1075, 1026,

[illegible] cm^{-1}

(b) Using sodium borohydride

To dimesitylene iron tetraphenylborate (2 g. 0.0024 mole) in ethylene glycol dimethyl ether was added sodium borohydride (5 g.) in small portions. The mixture was stirred for two hrs. Petrol (40°-60°) (100 ml) was added. The organic layer was washed with water (25 x 2) and dried (anhydrous $CaCl_2$). It was concentrated and chromatographed on alumina. The petrol (40°-60°) yielded bis(1,3,5- trimethyl- -cyclohexa- dienyl)iron (0.24 g. 37%) identified by infrared spectral comparison with an authentic sample.

Reaction of the dimesitylene-iron cation with sodium borohydride.

A mixture of freshly prepared ferrous chloride (2 g. 0.0158 mole), anhydrous aluminium chloride (3 g. 0.0225 g.) and pure dried mesitylene (80 ml) was refluxed for 6 hrs. The colour of the solution turned reddish brown. It was cooled in ice and sodium borohydride (5 g.) suspension in ethylene glycol dimethyl ether (50 ml) was added in small portions. The red colour changed to orange. Petrol (40°-60°) (50 ml) and organic layer was washed with water (100 ml) and dried ($CaCl_2$ anhydrous). On evaporation of the solvent yellow crystals of bis(1,3,5- trimethyl-cyclohexadienyl)iron (0.04 g.) m.p. 126° were obtained, identified by m.p. and infrared spectral comparison with an authentic sample.

Attempted reaction of tritylfluoroborate with bis(1,3,5 trimethyl- - - - cyclohexadienyl)iron

A solution of tritylfluoroborate (0.4 g. 0.00121 mole) in methylene chloride (5 ml) was added to a solution of bis(1,3,5 trimethyl- - cyclohexadienyl)iron (0.2 g. 0.00068 mole) in methylene chloride (5 ml) After a few minutes an orange precipitate of dimesitylene-iron di-tetrafluoroborate was (0.23, 73%) separated, identified by its infrared spectrum.

Attempted reaction of the dibenzene-iron cation with sodium borohydride

A mixture of freshly prepared ferrous chloride (2 g. 0.0158 mol), aluminium chloride (anhydrous) (3 g. 0.0225 mole) and pure thiophene free benzene (80 ml) was refluxed for six hours. The colour of the solution turned reddish brown. After cooling the solution, sodium borohydride (5 g.) was added in small portions in ethylene glycol dimethyl ether (50 ml). A vigorous reaction took place. The mixture was stirred for half an hour. Petrol ($b.p._{40-60^{\circ}}$) (100 ml) was added and the organic layer was washed in water and dried ($CaCl_2$ anhydrous). After evaporation of the solvent under vacuum, an orange crystalline product (0.040 g.) was obtained. The infrared spectrum was superimposible on that of the product prepared by Williamson . The product could not be fully characterised due to its small yield.

I.R. ν_{max} 1960, 1810, 1595, 1471, 1449, 1370, 1033 cm^{-1}.

Preparation of cyclopentadienyl benzene iron triiodide[89]

A mixture of ferrocene (2 g.,0.0106 mole) anhydrous aluminium chloride (2.84 g., 0.0212 mole) and aluminium powder (0.28 g., 0.0106 g.atom) and thiophene free benzene (80 ml.) was refluxed for 8 hrs. The colour of the mixture changed from orange to yellowish brown. Water was added carefully after cooling the reaction mixture and stirred vigorously. The water layer was separated and washed with petrol (b.p. 60-80) and a solution of potassium iodide and iodine (5:1) in water was added. The orange precipitate of benzene cyclopentadienyl triiodide (3.5 g.) m.p. 228°C. (Lit. m.p. 226-227°) was dried and recrystallized from acetone (m.p. 230°).

Preparation of benzene cyclopentadienyliron iodide.[89]

A solution of cyclopentadienyl benzene iron triiodide (5 g.) in ethanol (100 ml.) was treated with sodium thiosulphate in excess. The mixture was boiled for 15 minutes and filtered under nitrogen. The solvent was removed under vacuum in nitrogen. The yellow crystals (3 g.) of cyclopentadienyl benzene iron iodide were recrystallized by chloroform (m.p. 228°). (Lit 230-230.5°).

Preparation of cyclopentadienyl cyclohexadienyliron[66]

(a) Using lithium aluminium hydride.

To benzene cyclopentadienyliron triiodide (5 g.) in ethylene glycol dimethyl ether (50 ml.) lithium aluminium hydride (2 g.) was added in small portion and the mixture was stirred for one hour. The colour of the solution turned red with vigorous reaction. Methanol (10 ml.) was carefully added and then water (100 ml.). After addition of petrol (b.p. 60-80°)(50 ml.), the organic layer was washed with water (50 x 2) dried (anhydrous $CaCl_2$) and chromatographed on neutral alumina. The only orange red band eluted with petrol (b.p. 60-80°) afforded cyclohexadienyl cyclopentadienyl (.7 g.) as red crystal (m.p. 135°C).

(b) Using sodium borohydride.

Benzene π-cyclopentadienyliron triiodide (1 g.) in ethylene glycol dimethyl ether (50 ml.) was treated with sodium borohydride (5 g.) in small portions. The reaction mixture was stirred for one hour, water was added carefully. After addition of petrol (b.p. 60-80°) (50 ml.), the organic layer was washed with water, dried (anhydrous $CaCl_2$) and concentrated to small bulk. It was chromatographed on neutral alumina. An orange red band on elution with petrol (b.p. 60-80°) yielded cyclohexadienyl cyclopentadienyliron (.13 g.,) identified by comparison of infrared spectrum with an authentic sample.

Preparation of methyl-cyclohexadienyl cyclopentadienyliron

A solution of methyl lithium (prepared by lithium (0.07 g. 0.01 mole) and freshly distilled methyl iodide (1.42 g. 0.01 mole) in ether (50 ml.) was added to a suspension of cyclopentadienyl benzene iron iodide (1.6 g. 0.005 mol) (25 ml.) at -40°C. The mixture was stirred one hour. It turned reddish yellow. The solvent was removed under vacuum. The residue was extracted with petrol (b.p. 30/40) and ether. The extract was concentrated and chromatographed in neutral alumina (deactivated for three hours).

An orange band eluted by petrol (b.p. 30-40°) gave orange oil (0.030 g.) of methexyl cyclohexadienyl pentadienyliron. It was not characterised due to its small yield.

I.R. ν max. 3030(Sh) 2941(Sh) 2924(Sh) 2857(Sh) 1471(w) 1445(m) 1408(w) 1389(m) 1351(m) 1305(m) 1266(w) 1136(w) 1099(S) 1010(Sh) 995(b.Sh) 855(b) 806(b.Sh).

Attempted reaction of sodium methoxide with (benzene) cyclopentadienyliron iodide

A solution of (benzene) cyclopentadienyliron iodide (1 g., 0.003 mole) in absolute methanol (100 ml.) was added to a solution of sodium methoxide prepared from sodium (0.08 g., 0.003 mole). The mixture was stirred overnight but no change of colour was observed. The solvent was removed in vacuo and the residue was extracted with petrol (b.p. 40-60°) benzene and methanol.

The yellow extract from methanol gave only unreacted cyclopentadienyl benzene iron iodide (0.86 g. 80%) identified by infrared spectral comparison with an authentic sample.

Attempted reaction of potassium tertiary butoxide with benzene cyclopentadienyliron iodide.

Fresh sublimed potassium tertiary butoxide (1.12 g., 0.01 mole) in tetrahydrofuran (50 ml.) was treated with benzene cyclopentadienyliron iodide, (2 g.) and the mixture was stirred overnight and filtered. The solvent was removed under vacuum. The residue was extracted with petrol (b.p. 40-60°), benzene and methanol separately. Only methanol extract gave unreacted benzene cyclopentadienyliron iodide (1.7 g.) identified by infrared spectral comparison with an authentic sample.

Attempted acetylation of cyclopentadienyl cyclohexadienyliron

A solution of freshly distilled acetyle chloride (0.5 g.,0.0065 mole) in methylene chloride (10 ml.) was added in aluminium chloride anhydrous (0.5 g.) and the mixture was stirred for 30 minutes. The solution was quickly filtered through a suction pump and was added to a solution of cyclohexadienyl cyclopentadienyliron (1 g.) in small portion at 0^{o}C. The colour of the solution changed from red to yellowish brown. After 15 minutes the solvent was removed under vacuum and extracted with petrol b.p. ($30-40^{o}$) and ether and then water. The ether extract was concentrated and chromatographed in neutral alumina. The only orange band yielded ferrocene (0.24 g.) identified by infrared spectral comparison with an authentic sample.

The water extract on treatment with a solution of sodium tetraphenyl-borate in excess afforded yellow crystals of cyclopentadienyl benzene-iron tetraphenyl borate (0.43 g.) identified by infrared spectral comparison with an authentic sample.

Preparation of cyclohexene dicarbonyl π-cyclopentadienyliron hexafluorophosphate[54]

A solution of bromodicarbonyl-π-cyclopentadienyliron (2.56 g. 0.01 mole) in cyclohexene (200 ml) was treated with anhydrous aluminium bromide (6.46 g. 0.024 mole) and stirred vigorously for three hours. The red solution was separated into two layers. The upper layer containing cyclohexene was separated from a red viscous mass. It was hydrolised by ice water. The orange water solution was filtered through Kieselguhr. It was treated with excess ammonium hexafluorophosphate solution. The yellow precipitate of cyclohexene dicarbonyl π-cyclopentadienyliron hexafluorophosphate was filtered, dried and recrystallised by acetone/ether to give golden yellow crystals (2 gm. 50%) m.p. 150°
(Lit. 146° yield 38%).

Cyclohexane dicarbonyl cyclopentadienyliron

A suspension of cyclohexene dicarbonyl cyclopentadienyliron hexafluorophosphate (1 g. 0.0025) in tetrahydrofuran (25 ml) was treated with sodium borohydride (2 g.). The colour changed from yellow to brown. The mixture was stirred for 30 minutes. The solvent was removed and the residue was extracted with petrol (b.p. 30-40°) and chromatographed on neutral alumina.

A brown band was eluted with petrol (30-40°)/ether (1:1) yielded a brown oil of σ-cyclohexanedicarbonyl cyclopentadienyliron (0.32 g. 50%) purified by distillation at 75°/0.001. It was found too unstable to give

correct analysis.

I.R. ν max. 2915, 2840 (VS.Sh), 2000 (VS), 1940 (VS), 1440 (S), 1412 (Sh), 1340 (m.Sh), 1240 (m), 1255 (Sh), 1150 (m), 1155 (Sh), 1030 (m) 1010 (Sh), 990 (Sh), 980 (Sh), 860 (m), 830 (Sh), 820 (VS), 795 (W. Sh)

Attempted reaction of σ- cyclohexane dicarbonyl π-cyclopentadienyliron with tritylfluoroborate.

A solution of tritylfluoroborate (0.3 g. 0.001 mole) in tetrahydrofuran (2 ml) was treated with a solution of cyclohexane dicarbonyl cyclopentadienyl iron (0.1 g. 0.0004 mole) in tetrahydrofuran (5 ml). After shaking the solution for a few minutes a few drops of water were added to destroy tritylfluoroborate. The yellow crystals of cyclohexane dicarbonyl cyclopentadienyliron tetrafluoroborate (0.15 g. 11%) were separated on addition of ether in excess. It was crystallized by acetone/ether (m.p. 200°).

I.R. ν max 3125, 2837, 2128, 2062, 1408, 1124-1000, 962, 833 cm^{-1}

Reaction of potassium iodide with cyclohexane dicarbonyl π-cyclopentadienyl iron hexafluorophosphate.

Cyclohexane dicarbonyl cyclopentadienyliron hexafluorophosphate (0.4 g. 0.001 mol) solution in acetone (100 ml) was treated with potassium iodide (0.2 g. 0.0012 mole). The mixture was stirred for three hrs. The colour of the solution changed from yellow to brown. The solvent was removed under vacuum. The brown residue was extracted with petrol (b.p. 30-40°) ether and benzene. The extract was concentrated and chromatographed on

neutral alumina. The black brown crystals (0.15 , ,56%) of iodo-dicarbonyl cyclopentadienyliron . . were obtained by eluting the brown band with ether/benzene (1:1), identified by its m.p., mixed m.p. and infrared spectrum which was found superimposible with that of an authentic sample.

Attempted reaction of potassium cyanide with cyclohexene dicarbonyl cyclopentadienyliron hexafluorophosphate

(In Methanol)

(a) To a solution of cyclohexene dicarbonyl cyclopentadienyliron hexafluorophosphate (0.4 g. 0.00099 mole) in methanol (50 ml) was a solution of potassium cyanide (0.1 g. 0.000246 mole). The mixture was stirred for one hr. The orange red solution turned yellow. The solvent was removed under vacuum. The residue was extracted with petrol (30-40°) benzene and chloroform. The yellow extract was concentrated and chromatographed on alumina. The yellow band was eluted with ether/benzene (1:1). It afforded yellow crystals (0.085 g. 42.35%) m.p. 119°C identified as cyano-dicarbonyl cyclopentadienyliron on the basis of m.p. mixed m.p. and infrared spectrum comparison with an authentic sample.

(b) In acetone

To a solution of cyclohexene dicarbonyl cyclopentadienyliron hexafluorophosphate (0.4 g. 0.0009 mole) in acetone (25 ml) was added potassium cyanide (0.1 g. 0.0015 mole). The mixture was removed in vacuo and the residue was extracted with petrol (30-40°), ether and benzene. The extract

was concentrated and chromatographed.

A yellowish brown oil was (0.04 g.) eluted by ether/benzene. The oil decomposed during distillation and could not be fully characterized.

I.R. ν max. 2154 (m), 2083 (S), 2041 (S)

The second fraction eluted by benzene/chloroform gave yellow crystals of cyanodicarbonyl cyclopentadienyliron identified on the basis of its infrared spectral comparison with an authentic sample.

I.R. ν max. 2125, 2060, 2020

Attempted reactions of phenyl lithium with cyclohexene dicarbonyl cyclopentadienyliron hexafluorophosphate

(a) Phenyl lithium (0.001 mole)prepared by lithium (0.007 g. 0.001 mole) and bromobenzene (0.157 g. 0.001 mole) in ether (50 ml) was added to a suspension of cyclohexene dicarbonyl cyclopentadienyliron hexafluorophosphate (0.4 g. 0.00092 mole) in ether (25 ml) at $0^{\circ}C$. The mixture turned reddish brown. It was stirred for one hr. The solvent was removed under vacuum. The residue was extracted with petrol ($30-40^{\circ}$), ether and benzene. The extract was concentrated. and chromatographed on neutral alumina.

A yellow oily residue was eluted in traces.

A main red band on elution with petrol ($30-40^{\circ}$)/ether gave a red crystalline compound (0.012 g.) m.p. 122°. It could not be fully characterized.

I.R. ν max. 2933, 2857, 2083, 2000, 1408, 1000, 869, 837 cm^{-1}

(b) Phenyl lithium was prepared in twofold excess by taking lithium (0.04 g. 0.0058 mole) bromobenzene (0.8 g. 0.0051) and in ether (100 ml.) and was added to the suspension of above mentioned salt (1 g. 0.0025) in ether (25 ml.) at -70°C. The salt was quickly dissolved and the colour of the solution turned yellowish brown. The reaction mixture was stirred 15 minutes. The solvent was removed and the residue was extracted with petrol (b.p. 30-40°), ether and benzene.

The extract after concentration was chromatographed on neutral alumina.

A yellow oily residue in traces was eluted by petrol (b.p. 30-40°). It was not characterised due to its small yield. I.R. shows no absorption in metal carbonyl region.

A main yellow band eluted by petrol (b.p. 30-40°)/ether (1:1) yielded brownish yellow oil (0.48 g.) purified by distillation at 100°/0.005 mm.

Analysis found	C, 66.7;	H, 4.4;	O, 13.2
	66.6;	4.5;	
$C_{20}H_{14}FeO_3$ requires	C, 66.5;	H, 4.4;	O, 13.2

I.R. ν_{max} 2020, 1980, 1655, 730, 700 cm^{-1}

The third band afforded brown crystals (0.042 g.) of tetracarbonyl dicyclopentadienyl diiron identified by infrared spectral comparison with an authentic sample.

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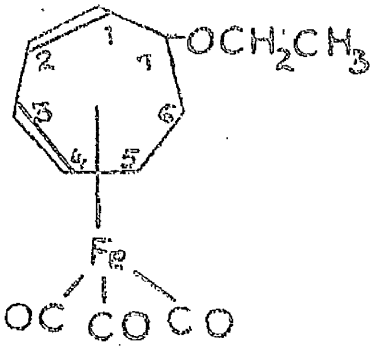
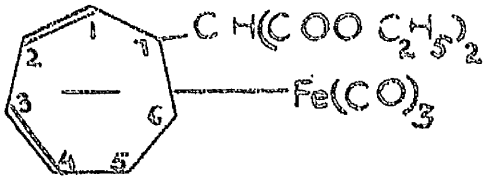
APPENDIX

N.M.R. Spectra



τ, Value	Multiplicity	Relative Intensity	Assigrment
4.7	Multiplet	2	H_2, H_3
6.7	Quartet	5	CH_2 } of ethoxy group
8.9	Triplet		CH_3 } $J = 7$ c/s
6.2-7.4	Multiplet	3	H_1, H_4, H_7
7.6-9.0	Multiplet	4	H_5, H_6

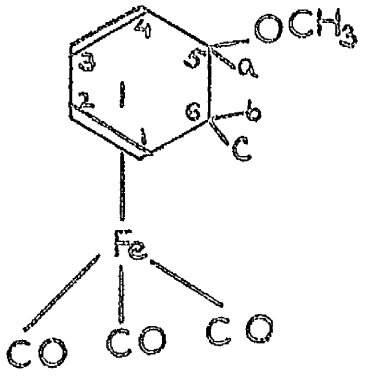
N.M.R. Spectra



Values	Complexity	Relative Intensity	Assignment
4.2 - 5.0	Multiplet	*	H_2, 3
5.6 - 6.3	Multiplet		$2CH_2$ of ethyl + H_7
6.8 - 7.5	Broad band		H_1, H_4, H_7
7.8 - 8.6	Broad band		$2H_5$, $2H_6$
8.7 - 9.2	Multiplet		$2CH_3$ of ethyl

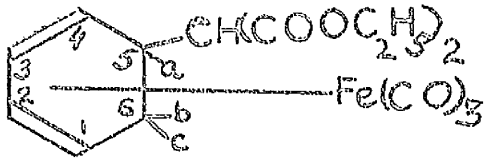
* Relative intensities were reasonably consistant with the above structure and assignments but due to the very complex nature of the signals, specific values could not be deduced .

N.M.R. Spectra



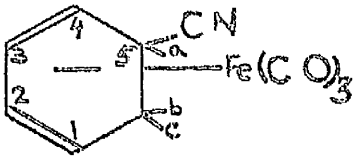
τ Value	Multiplicity	Relative Intensity	Assignment
4.55	Multiplet	2	H_2, H_3
6.25	Multiplet	1	H_{5a}
6.5-7.5	Complex Multiplet	2	H_1, H_4
6.85	Singlet	3	OCH_3
8-8.3	Complex	2	Hb, Hc

N.M.R. Spectra



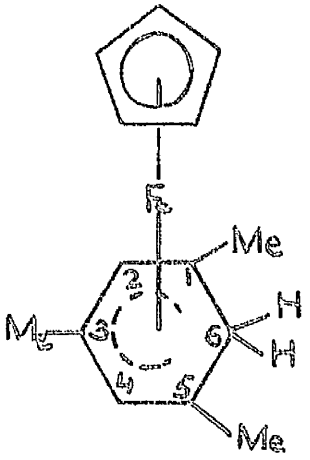
τ Value	Multiplicity	Relative Intensity	Assignment
4.7	Triplet	2	H_2, H_3
5.9	Double quartet	4 + 1	2 $>CH_2$ of $-C_2H_5$ group + Ha.
6.9	Complex	2	H_1, H_4
8-8.0	Complex	2	Hb, Hc
8.8	Double Multiplet	6	2 CH_3 of ethyl group J = 7c/s

N.M.R. Spectra



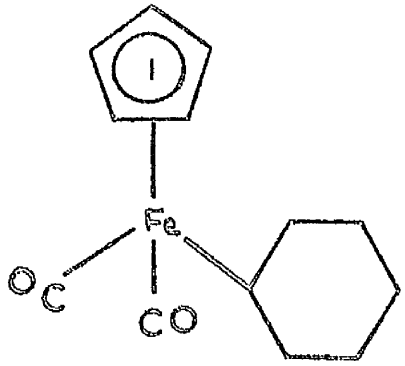
τ Value	Multiplicity	Relative Intensity	Assignment
4.45	Multiplet	2	H_2, H_3
6.8-7.1	Complex Multiplet	3	Ha, H_1, H_4
7.3-8.1	Complex Multiplet	2	Hb, Hc

N.M.R. Spectra



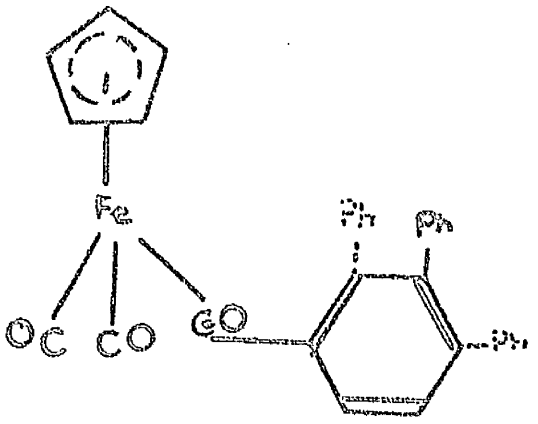
Value	Multiplicity	Relative Intensity	Assignment
8.61	Singlet	6	1,5 CH_3 groups
7.51	Singlet	3	3-methyl group
6.1	Singlet	5	5 Cyclopenta-dienyl protons
8-9	Unresolved	4	Remaining 4 protons

N.M.R. Spectra



τ- Value	Multiplicity	Relative Intensity	Assignment
5.40	Singlet	5	5 Protons of cyclopenta-dienyl group
8.0-9.0	Complex	11	Cyclohexyl group

N.M.R. Spectra



τ Value	Multiplicity	Relative Intensity	Assignment
5.27	Singlet	5	Cyclopentadienyl protons
2.1-3.4	Complex Multiplet	9	Diphenyl protons

Table 1. Iododicarbonyl π-dienyliron complexes

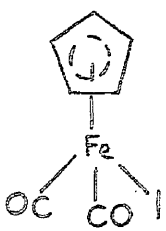
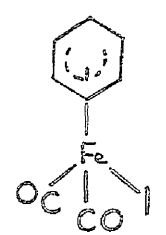
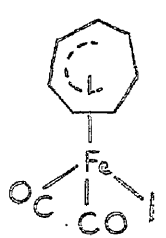
Compound	m.p.	Infra Red: C–H Stretch	Infra Red: M–C–O Stretch	Infra Red: Characteristic Band	Solubility	Reference
	Black crystals 117–118°C	3085(w)	2044(VS) 2000(VS)	1428(S) 1360(w) 1050(vw) 1017(vw) 1050(w) 1007(m) 860(mSh) 843(VS,broad)	Soluble in acetone chloroform benzene	80
	Red Brown crystal 95–96°	KCl disc. 2941(W) 2849(w)	2041(VS) 1992(VS)	1445 1404(m) 1316(W) Broad 1292(m) 1175(W) 1149(m) 1031(m) 1038(m) 999(m) 972(m) 926(b.m) 843(S) 791(S)	Soluble in acetone, chloroform benzene	Present work
	Maroon crystal 90–91°	KCl disc 2941–2849 (w.broad)	2041 VS(CO) 1992 VS(CO)	triple 1449, 1429, 1404(W.broad) 1353(m) 1189(m) 1111(w.b.) 1070(v.b.) 1026(m) 1010(m) 970(w) 927(m.b) 965–854(m.(b)) 819(w) 806(w)	Soluble in acetone, chloroform benzene	70

Table 2. Cyano-dicarbonyl-π-dienyl complexes of iron

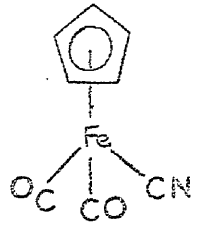
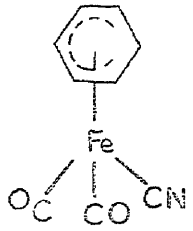
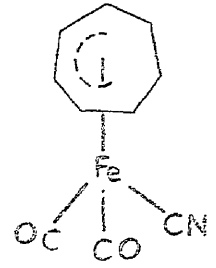
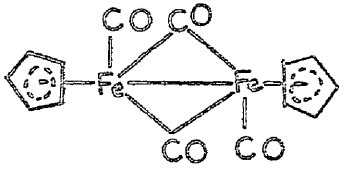
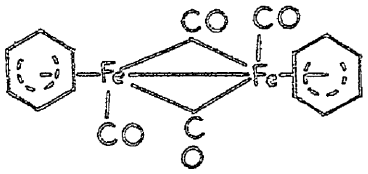
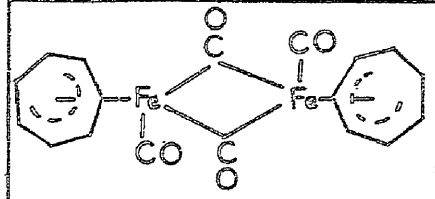
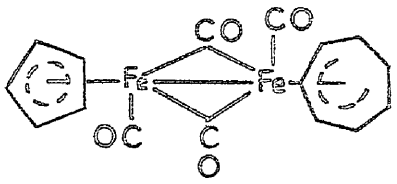
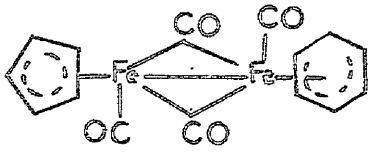
Compound	m.p.	Infra-red Spectra: C - H Stretch	Infra-red Spectra: M - CN Stretch	Infra-red Spectra: C - O Stretch	Infra-red Spectra: Other Characteristic Bands	Solubility	Reference
	Yellow crystal 120° dec.	3120(m)	2125(VS)	2060(VS) 2020(VS) 1003(S)	1420(m) 1360(w) 115(w) 1060(w) 1010(S) 854(S)	Chloroform Benzene Water	79
	Pale yellow crystal 90-91° (decomp.)	3030(W) 2941(W.b) 2817(m)	2128(VS)	2041(VS) 1992(VS)	1449(m) 1404(m) 1316(w) 1299(S) 1163(W.Sh) 1136(W.Sh) 1075(W.Sh) 1043(m) 1001(w) 991(S) 935(S) 895(S) 877(S) 800(S)	Chloroform Benzene decomposes in water, in air	Present Work
	Orange crystal 75-76° (decomp.)	3060(m) 3000(m) 2960(W) 2900(W) Sh 2840(m)	2137(VS)	2040(VS) 1980	1511(w) 1471(S) 1449(S) 1410(S) 1370(S) 1335(w) 1316(m) 1139(s) 1122(m) 1073(m) 1040 1021(m.Sh) 1000(w) 975(m) 956(m) 881(VS) 869(V.S.Sh) 832(m) 812(m)	Chloroform Benzene Methylene Chloride decomposes in air, water	Present Work

Table 3 Tetracarbonyl π-Dienyldiiron Complexes

	m.p.	Infra-red C - H ; C - O Stretching frequencies (cm^{-1})	References
	194	2000(Sh.W) 1965(VS) 1950(VS) 1770(VS) 1782(VS)	79
	134°C (dec.)	3030 W.Sh 2930 2825(W) 1976(VS) 1745(VS)	Present Work
	198°C	2985(W) 2865 (W) 2849 (Sh) 1972(VS) 1938(VS) 1736(VS)	Present Work
	168-170°C	3125(W) 2941 (W) 2857 (Sh) 1992(VS) 1946(VS) 1751(VS)	Present Work
	Decomp.	3030(W) 2941 (Sh) 2857 (Sh.W) 1980(VS) 1770(VS)	Present Work

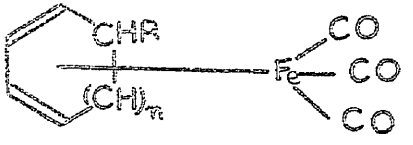


Table 4

n	R	Infra-red spectra
1	-H	3044(w) 3004(m) 2928(S) 2904(S) 2844(m) 2050(VS) 1976(VS) 1469(S) 1454(w) 1432(m) 1429(w) 1403(m) 1337(S) 1318(w) 1267(m) 1237(w) 1179(S)
2	-H	3026(S) 2975(S) 2918(S) 2875(S) 2840(S) 2046(VS) 1977(VS) 1458(S) 1447(S) 1442(S) 1404(S) 1372(m) 1348(S) 1338(S) 1262(w) 1225(w) 1194(w) 1163(m) 1090(m) 1060(S) 958(m) 933(w) 868(S) 843(m) 799(w) 641(w)
1	$-OCH_3$	3000 2980 2921 2882 2818 2020(VS) 1988(VS) 1470 1430 1400 1350 1270 1210 1180 1150 1120 1090 1075 1010 1000 940 909 860
2	$-OC_2H_5$	2941(S) 2857(S) 2062(VS) 1961(VS) 1449(S) 1389(w) 1370(m) 1325(S) 1299(w) 1266(w) 1220(w) 1163(m) 1111(S) 1090(m) 1087(m) 1075(m) 1064(S) 1042(m) 1000(S) 926(m) 909(w) 970(w) 855(m) 833(w) 800(m)
1	$-CH(COOEt)_2$	2967 2604 2857 2849 2053(VS) 2000(VS) 1996(VS) 1754 1724(VS) 1449 1408 1389 1368 1299 1147(bSh) 1089 1031 858
2	$-CH(COOEt)_2$	2941 2564 2053 2000 1996 1754 1724 1449 1408 1389 1389 1368 1299 1148 1091 1063 1031 858
1	-CN	3021 2941 2237 2045(VS) 1980(VS) 1451 1429 1389 1329 1297 1190 1148 1112 1011 1000 926 884 855 833
2	-CN	2941 2857 2237 2083(VS) 2247 2198(VS) 1460 1441 1429 1370 1325 1299 1280 1238 1220 1198 1176 1149 1087 1040 1019 990 965 904 890 847 826 794 751

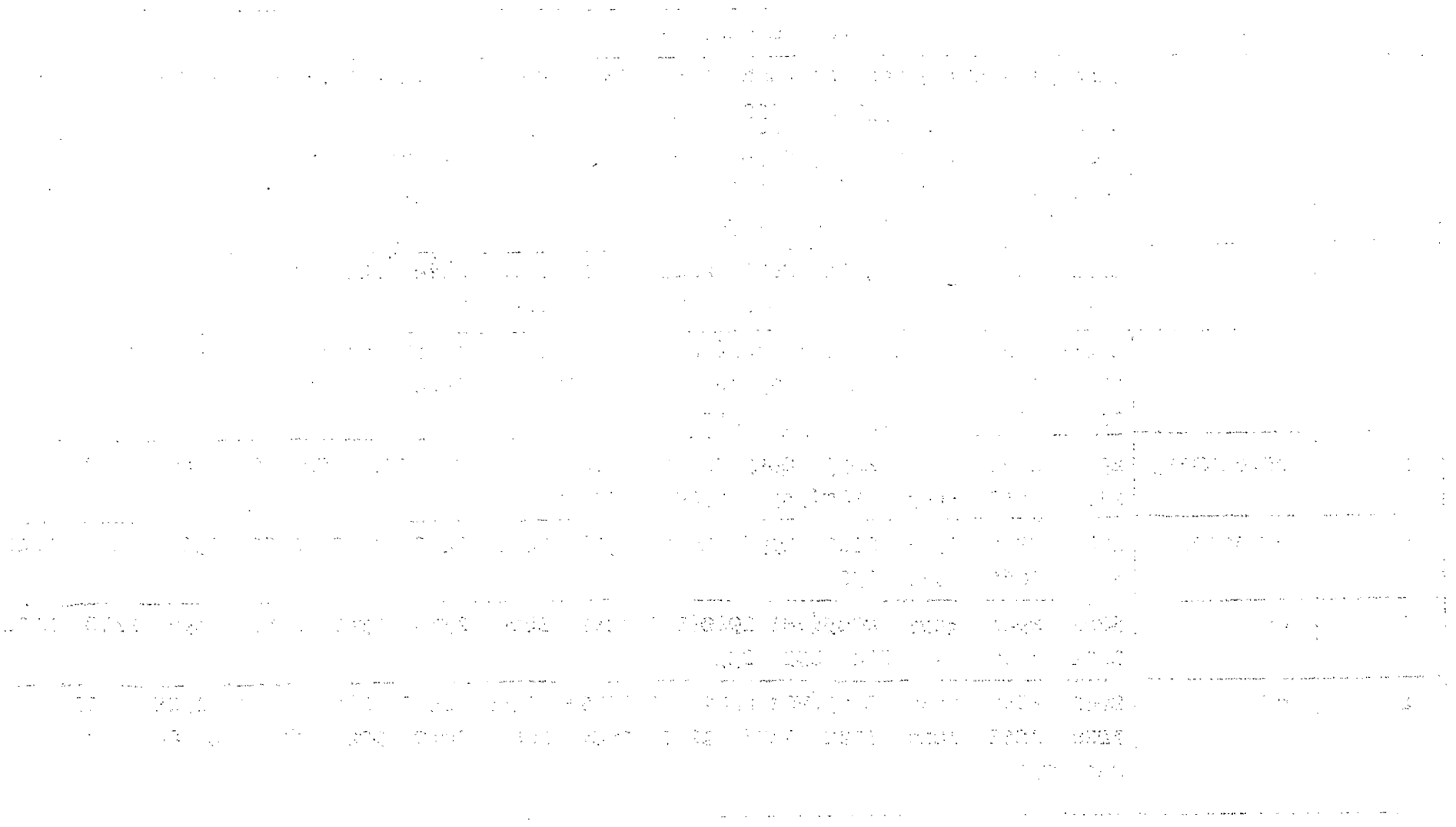
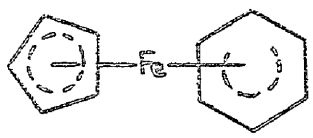
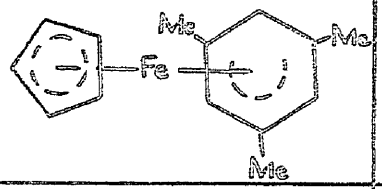
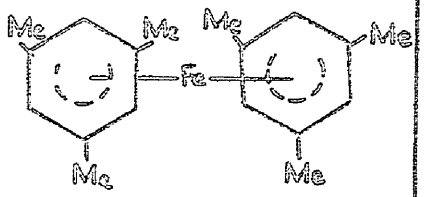
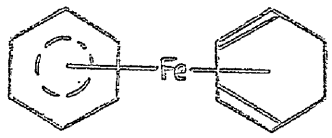


Table 5

Complex	Infra-red Spectra.
	3850(vw) 2525(w) 2430(w) 2055(w) 2020(w) 1981(m) 1960(m) 1882 (vw) 1837(vw) 1798(vw) 1772(w) 1716(w) 1688(w) 1653(m) 1624(m) 1483(m) 1445(w) 1420(w) 1394(w) 1316(w) 1290(S) 1175(w) 1138(w) 1105(S) 1053(S) 1001(S) 946(m) 939(m) 906(w) 843(S)
	3922(w) 3077(m.Sh) 2941(VS) 2857(Sh) 2740(VS) 1754(m) 1695(w) 1600(S) 1515(w) 1449-1429(VS) 1370(VS) 1299(S) 1244(w) 1163(w) 1099(VS) 1036(VS) 1031(Sh) 1000(VS) 962(S) 917(w) 873 854.7(w) 833(S.Sh) 800(VS) 682(m)
	2941 - 2857(VS) 1515(m) 1447(S) 1408(m) 1370-1365(S.Sh) 1290(m) 1220(w) 1075(S) 1026(VSO 990(m) 852(m) 833(m.Sh)
	2865, 2817, 1842, 1773, 1648, 1425, 1253, 1227, 1167, 1062, 1023, 1000, 974, 890, 874, 855, 847, 788

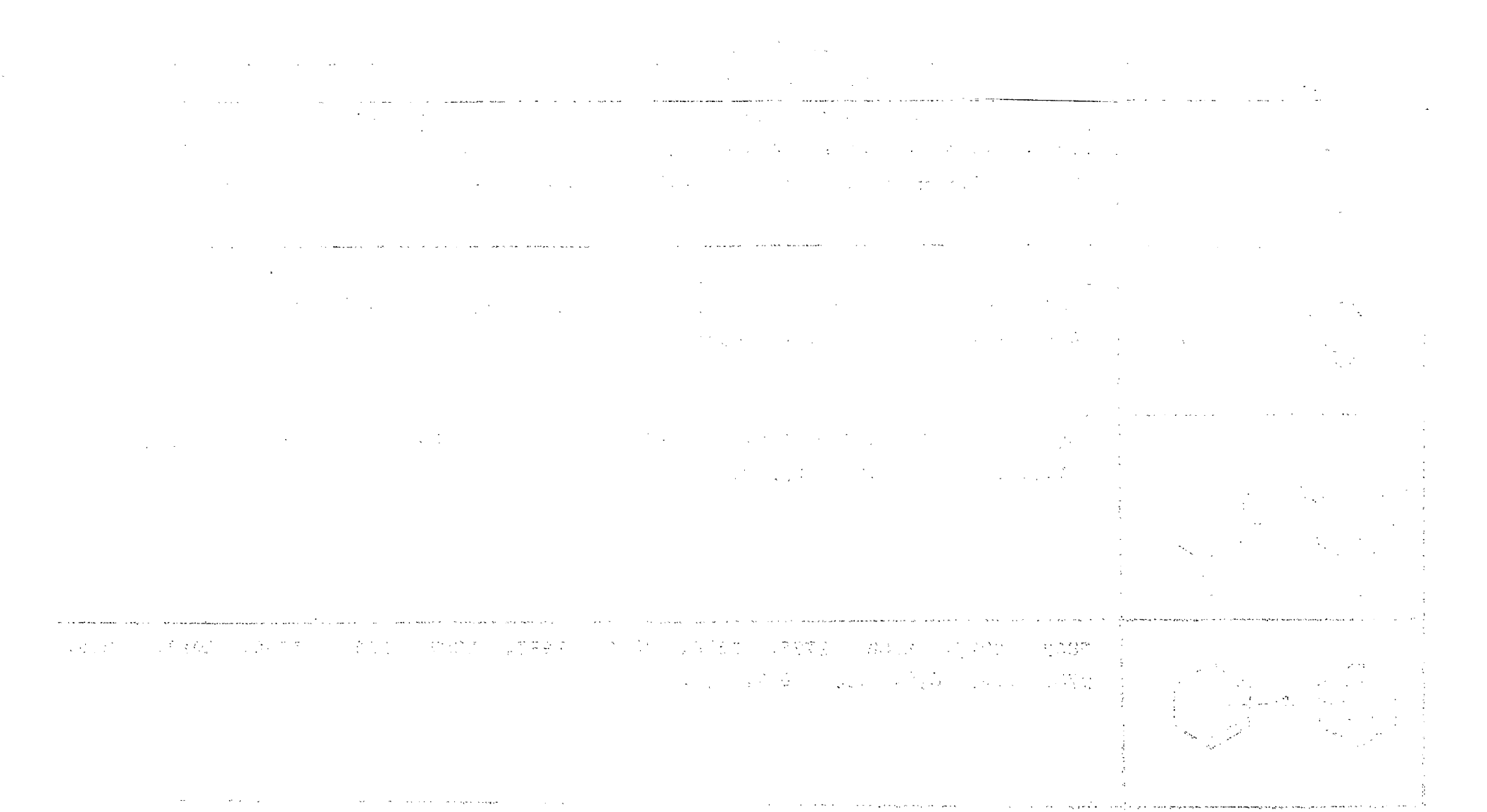
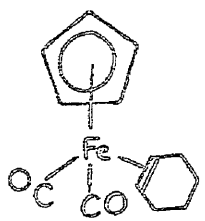
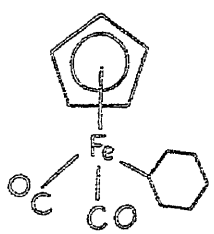
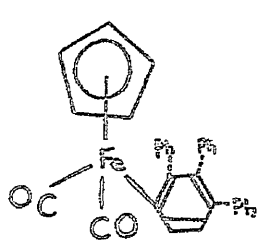


Table 6

COMPOUND	INFRARED SPECTRA
	3390 3106 2941 2857 2062 2016 1515 1441 1427 1387 1350 1264 1217 1155 1136 1112 1042 1010 966 922 877 855 769
	2915(VS) 2840(S) (Sh) 2000-1990(VS) 1950-1920(S) 1440(S) 1412(m.Sh) 1340(Sh) 1240(m.Sh) 1150(m) 1030(m) 1010(m) 990-980(m) 860(m) 830(Sh.m) 820(VS) 795(W.S)
	3100(m.Sh) 3050(S) 2960(W) 2910( )(Sh) 2200(VS)(1980-1950) 1655(S) 1595(m) 1560(V.S) 1480(m.Sh) 1470(V.S) 1450(m) 1440(m) 1435(m) 1350(w) 1315(m) 1270(S) 1180(w) 1160(w) 1060(m) 1050(m) 700(V.S) 940 (vm) 915(m) 840-830(S.Sh) 800(w) 780(w) 760(w) 730(V.S) 700(V.S)